Unconventional Superconductivity

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A brief review of unconventional superconductivity is given, stretching from the halcyon days of helium-3 to the modern world of Majorana fermions. Along the way, we will encounter such strange beasts as heavy fermion superconductors, cuprates, and their iron-based cousins. Emphasis will be put on the fact that in almost all cases, an accepted microscopic theory has yet to emerge. This is attributed to the difficulty of constructing a theory of superconductivity outside the Migdal-Eliashberg framework.

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I. INTRODUCTION TO UNCONVENTIONAL SUPERCONDUCTORS

Superconductivity was discovered in 1911 in an attempt to understand how the resistivity of a metal behaved at low temperatures (1). The ideas on the table were that the resistance would monotonically go to zero as absolute zero was approached, it would saturate, or it would diverge. One can imagine the surprise of Onnes' group when instead, the resistivity in mercury plummeted to zero at a particular temperature, T_c. Many famous theorists, including Einstein and Heisenberg, attempted to elucidate its origin, but it took the development of modern many-body theory in the 1950s before a proper toolkit emerged for its solution. Still, having the tools and coming up with a solution were two quite different things. It was the remarkable insight of John Bardeen coupled with the talents of a young postdoc, Leon Cooper, and an even younger student, Bob Schrieffer, that led to its ultimate solution (2), in the process beating out such luminaries as Lev Landau and Richard Feynman.

At the heart of the so-called BCS theory is the concept of Cooper pairs (3). What Cooper found was that an arbitrarily weak attractive interaction between electrons would lead to a profound rearrangement of the Fermi surface, leading to the formation of quasi-bound electron pairs. At a fell swoop, this solved many of the outstanding issues of superconductivity, particularly the existence of an energy gap. And, unlike fermions which typically do not condense, pairs of fermions, being statistically equivalent to bosons, can condense, which in turn can lead to a zero resistance state as well as to the famous Meissner effect (4; 5), where magnetic flux is expelled from a superconductor when going below T_c.

But Cooper pairs are very different from the real space pairs that had been suggested by Schafroth (6). Cooper pairs are constructed in momentum space, where one correlates an electron at $\mathbf{k}$ with its time reversed partner at $-\mathbf{k}$. In real space, these correlations extend out to a distance known as the coherence length which is typically much larger than the inter-particle separation. In momentum space, these correlations occur in an energy shell about the Fermi surface, very different from the Bose-Einstein condensation limit of real space pairs where the chemical potential is well below the bottom of the fermionic band.

Although the BCS theory is one of the most profound many body theories ever discovered in science, it is at heart a weak coupling mean field theory. Its great success followed two subsequent developments. The first was the realization by Gor'kov that the theory was equivalent to the more general Ginzburg-Landau theory based on a phenomenological order parameter (7). This opened up a large vista of applications, since the simplicity of that theory could be applied to a large variety of problems, including the spatial variation of the order parameter (8). The second was the realization by Migdal (9) that the success of BCS theory was based on the fact that a controlled perturbation expansion existed for the electron-ion interaction that was at the heart of the BCS mechanism. In essence, besides the repeated scattering of electrons that leads to the infrared Cooper singularity (the ladder sum shown in Fig. 1), all other Feynman diagrams are controlled by an expansion in the small parameter $\hbar\omega_D/E_F$, where ω_D is the Debye frequency of the

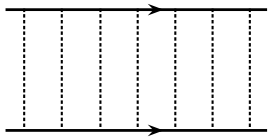

FIG. 1 Particle-particle ladder sum that gives rise to the Cooper instability. Solid lines are electrons, dashed lines the pair interaction.

ions, and E_F the Fermi energy of the electrons. This led to the generalization of the BCS theory by Nambu (10) and Eliashberg (11) to take into account the frequency dependence of the normal and anomalous (pairing) self-energies.

The resulting strong coupling theory was developed by Schrieffer and colleagues (12) into a precise formalism for describing pairing in real systems. The success of this theory was the prediction of anomalies in tunneling spectra caused by the frequency dependence of the pairing self-energy associated with phonons that essentially proved that conventional superconductivity originated from the electron-ion interaction (13; 14). The theory also resulted in a quantitative tool for estimating superconducting transition temperatures (15; 16). From this, one can understand what limits conventional superconductivity to relatively low temperatures (17). In BCS theory, the underlying mechanism is the electron-ion interaction. An electron polarizes the surrounding lattice of ions. Since the ion timescale is much slower than the electrons (as they are much heavier), the polarization cloud persists as the electron moves away. A second electron can then move in and take advantage of this attractive polarization cloud (Fig. 2). This is how the electrons can indirectly attract each other despite the large Coulomb repulsion between them. In essence, the electrons avoid the Coulomb repulsion by being at the same place, but at different times. There are two consequences of this. First, the electrons are in a relative s-wave pair state (which is a spin singlet due to fermion antisymmetry). Second, the large Coulomb repulsion is renormalized to a smaller value when projecting from an energy scale E_F down to a scale $\hbar\omega_D$ (18), thus allowing a net attraction, but the resulting 'retardation' limits T_c.

But not all were so impressed by these developments. The famous experimental physicist Bernd Matthias was well known for his negative opinion of BCS theory and its strong coupling avatars. This came from a lack of prediction for any new superconductors. The latter was not a surprise given the exponential dependence of T_c on microscopic parameters (a consequence of the logarithmic infrared singularity), but Matthias' opinion was that if the strong coupling theory was so precise as claimed by its various practitioners, why had it provided so little guidance to him and his experimental colleagues when searching for new superconductors? In some sense, he went too far in asserting that only simple non-transition elements like mercury and lead were within the sphere

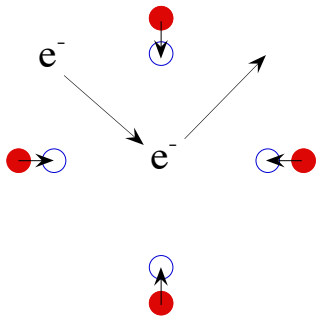

FIG. 2 The electron-ion interaction leads to an induced attraction between electrons. Arrows joining circles represent displaced positive ions that are attracted to the electron - the timescale for relaxation back to their original positions is slow compared to the electron dynamics, allowing a second electron to take advantage of this distortion.

of BCS theory (19). It is now generally recognized that transition metals such as niobium and its higher temperature A15 cousins like Nb_3Sn are well described by the Midgal-Eliashberg formalism (20). But the lack of predictability is definitely an issue. In that context, MgB_2 is a simple material that had been lying around for fifty years before it was discovered to be a high temperature superconductor (21). Subsequently, it was shown that standard strong coupling theory gave a good description of its properties (22). But even predictions based on this success did not pan out when looking for superconductivity in related materials (23). This emphasizes that we have a long way to go before even conventional superconductivity becomes a truly predictive science.

So having emphasized 'conventional', but do we mean by this and its counterpart 'unconventional'? In BCS theory, the pairing is mediated by the electron-ion interaction, leading to a relative pair state with s-wave symmetry. Anisotropy of the energy gap (which is proportional to the superconducting order parameter in BCS theory) in momentum space is relatively weak. But as soon realized after the BCS theory was published, it could be easily generalized. In BCS theory, the electron-ion interaction is transformed into an effective electron-electron interaction limited to a shell in momentum space around the Fermi surface. As such, any effective attractive interaction can be so treated, and it can even be extended to finite systems (such as the pairing of nucleons in nuclei due to the strong interaction, where the 'shell' in this case is the surface region of the nucleus (24)). Moreover, it can be easily generalized from an s-wave state to any other symmetry for the pair state. Therefore, by 'unconventional', we mean a pair state that is not an isotropic s-wave state, and where the interaction is something other than the conventional electron-ion interaction elucidated in the 1950s.

This brings us to ^{3}He.

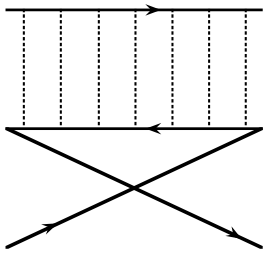

FIG. 3 Induced pair interaction from spin fluctuations (30). Note the particle-hole ladder sum, which gives rise to the dynamic spin susceptibility, embedded in this diagram.

II. HELIUM-3

The first unconventional material didn't turn out to be a superconductor at all, but rather a superfluid. As the BCS theory developed in the late 1950s and early 1960s, it was realized that it could be applied to a variety of interesting systems. It had already been known that ^{4}He underwent Bose condensation at low temperatures. But what about ^{3}He? As each atom is a fermion (two protons, a neutron, and two electrons), for it to condense, some kind of pairing must take place. But how? After all, these filled shell atoms have a large hard core repulsion. But at larger separations, an attractive van der Waals interaction exists. By pairing in a relative d-wave state, the atoms could avoid the hard core repulsion (since the d-wave state has a quadratic node at zero separation) and take advantage of the van der Waals tail (since the maximum of the d-wave state occurs in the tail region) (25).

But in the late 1960s, a different potential mechanism was proposed. To understand this one must go back to the early days of the BCS theory. Shortly after the BCS theory was published, Anderson realized that the state should survive even the presence of disorder, since one can always define time reversed states even if the momentum states are smeared due to impurity scattering (26). Magnetic impurities, though, were different, in that they flipped the spin and thus broke the singlets (27). In strong coupling theory, this pair breaking effect was easily generalized to inelastic ferromagnetic spin fluctuations (28). But Fay and Layzer (29) realized that this argument could be turned around to argue that ferromagnetic spin fluctuations could mediate spin-triplet p-wave pairing (Fig. 3). In essence, an 'up' spin would prefer to have neighboring 'up' spins, thus leading to an induced attraction due to exchange forces. They predicted that this could be the case for nearly ferromagnetic palladium (never realized, at least yet) as well as for ^{3}He.

Regardless, the discovery of superfluidity in ^{3}He in 1972 was a surprise (31). The experimentalists were actually looking for magnetism (which was subsequently found (32)). But what rapidly emerged was that they had indeed found p-wave superfluidity (33). And, it turned out that there were *two* superfluid phases. The main phase was the so-called B phase, first described theoretically by Balian and Werthamer (34). In this phase, the pair state is of the form $k_x\hat{x} + k_y\hat{y} + k_z\hat{z}$ where $\hat{x}$, for instance, means that the projection of the Cooper pair spin along this axis is zero (these three spin components form a vector known as the d vector). Since the Fermi surface is a sphere, this function leads to an isotropic energy gap. But, in a narrow sliver of temperature and pressure, another phase known as the A phase exists. This phase, first theoretically described by Anderson and Morel (35) has the form $(k_x + ik_y)\hat{z}$. This function has zeros (nodes) at the north and south 'poles' of the Fermi surface, leading to a highly anisotropic energy gap.

The existence of the A phase was a surprise, since a simple Ginzburg-Landau (G-L) treatment would predict that the B phase would always be stable. The reason is that its isotropic gap maximizes the free energy gain due to superfluidity (easily seen by evaluating the quartic term in G-L theory). A possible solution was offered by Anderson and Brinkman a year after the discovery of Osheroff, Richardson and Lee (36). In spin fluctuation models, the pair interaction is strongly influenced by the superconductivity itself. This is because the underlying fermion degrees of freedom become gapped, thus leading to a gap in the spin fluctuation spectrum, which in turn suppresses the pairing. This is very different from electron-ion theories, where the phonons do not become gapped (they do become less damped, of course, which does have a minor feedback effect on the pairing). Obviously, this suppression effect is less pronounced for the A phase, given its anisotropic gap, which acts to stabilize the A phase in a narrow temperature range (until this feedback effect is overwhelmed by the quartic term which grows as the temperature is reduced).

The Anderson-Brinkman theory could have been viewed as such a success, one might simply have declared victory and moved on. But life was not so simple for a variety of reasons. ^{3}He is a relatively simple system from a solid state physics perspective. It is a single band system with a simple parabolic dispersion, with weak spin-orbit effects. The normal state interaction parameters (so-called Landau parameters) are described by simple Legendre polynomials, and are well known from experiment. These parameters in turn determine the pairing interaction (37), which has been mapped to high precision (38). Analyzing in terms of physical interactions, one finds that everything and the kitchen sink contributes to the pairing, including not only spin, but also density and current fluctuations (39).

This complexity has led to much richness in microscopic theories designed to explain ^{3}He, which went on to play an important role after the subsequent discovery of unconventional superconductors. Strong coupling theories of spin fluctuations were developed to further improve our understanding of ^{3}He, and this led to one of the first occurrences of quantum criticality in the context of superconductivity (40). The idea was that as physical parameters such as pressure were tuned to approach

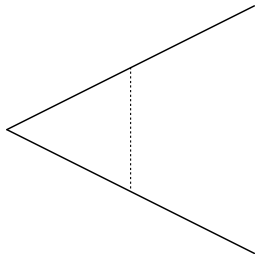

FIG. 4 Vertex correction (41). In electron-electron theories, this diagram can be as large as the lowest order self-energy ('rainbow') diagram, leading to a violation of Migdal's theorem.

the magnetically ordered state, T_c rose because of the increasing divergence of the pairing interaction, which in these models is proportional to the dynamic spin susceptibility. On the other hand, for the same reason, the energy scale of the spin fluctuations collapses as the critical point is approached. Eventually the latter effect wins out, and T_c, after achieving a maximum, is predicted to plummet to zero. On the other hand, it was also realized that the 'Migdal-Eliashberg' basis of such calculations was suspect. The reason is that the spin fluctuations are composed of the same electrons that one is pairing, unlike the electron-ion case where electrons and phonons can be considered as independent objects to a good precision. One might naively think that one can separate the 'slow' degrees of freedom (the spin fluctuations) from the 'fast' ones (quasiparticles), but explicit calculations find that vertex corrections can be of the same order as the lowest order 'rainbow' diagram (Fig. 4) in stark contrast to the electron-ion case (41). This casts doubts whether a controlled perturbation expansion can be constructed, and the similar fears have recently been realized in the context of nematic and antiferromagnetic spin fluctuations by Metlitski and Sachdev (42; 43). Besides spin fluctuations, other approaches have also been advocated, including the polarization potential model of Bedell and Pines (44).

The other interesting point is that the magnetic phase of ^{3}He is not a ferromagnet as centrally assumed in the spin fluctuation models. It actually is an antiferromagnet (45). This led to a rethinking of the problem. In particular, it was realized that in some sense, the atoms in superfluid ^{3}He are better described as nearly localized rather than nearly magnetic (46). These ideas provided some of the foundational basis of theories that would later be developed in the context of cuprates - in particular the idea of Gutzwiller projection (to suppress double occupation in the many body wavefunction) and the concept of using $1/d$ as an expansion parameter, where d is the spatial dimension (the basis for dynamical mean field theory).

Most importantly, ideas in ^{3}He paved the way for the next big development in unconventional superconductors - heavy fermions.

III. HEAVY FERMION SUPERCONDUCTORS

The discovery of heavy fermion superconductors again shows the hit and miss nature of the field of superconductivity. Arguably, these materials had been around for a number of years. Despite the general prejudice that magnetism was bad for superconductivity (27; 28), those like Matthias who were not enamored of the BCS theory thought otherwise. Matthias had found superconductivity in a number of uranium based intermetallics and pointed out the close connection of these materials with their ferromagnetic counterparts (47). One of their more interesting discoveries was U_2PtC_2 (47). But because elemental α-U was suspected of being a conventional superconductor (which it probably is), these results provoked less curiosity than they should have. Then, in 1975, Bucher and colleagues reported superconductivity in UBe_{13}, where the f electrons were nearly magnetic (48). But their feeling was that the superconductivity they observed was due to filaments of α-U in their samples.

It took the remarkable discovery of superconductivity in $CeCu_2Si_2$ by Frank Steglich and collaborators to finally realize that a new class of superconductors had been elucidated (49). By that time, it had been discovered that a number of rare earth and actinide intermetallics exhibited a linear T specific heat coefficient at low temperatures, typical of a Fermi liquid. The difference, though, was that its magnitude was huge, up to 1000 times that of copper. This indicated that the quasiparticles in such materials were strongly interacting, with the f electrons being both nearly localized and nearly magnetic. In some sense, this would have been the last place one might expected to find a superconductor. Moreover, Steglich's group realized that it was the heavy electrons themselves that were superconducting, since the jump of the specific heat at T_c was comparable to the normal state specific heat (this jump in BCS theory is proportional to the order parameter).

After Steglich's breakthrough, much progress was made. A few years later, the Los Alamos group discovered heavy fermion superconductivity in UPt_3 (50), and it was (re)discovered as well in UBe_{13} (51). At this point, the field really took off. Even U_2PtC_2 was realized to be one as well (52). UPt_3 had properties reminiscent of ^{3}He, with what looked to be a $T^3\ln T$ correction to the specific heat (as predicted by spin fluctuation theories). Moreover, the heavy quasiparticles formed a normal (though complex!) Fermi surface (Fig. 5), as revealed by quantum oscillation measurements (53). This was a real surprise at the time, since these measurements indicated that the f electrons participated in the Fermi surface given the latter's resemblance to simple band theory calculations which treated the f electrons as itinerant (54). Although over the years, alternate models of the Fermi surface were proposed, with some f electrons participating in the Fermi surface and others not (55), recent definitive results decisively verify the itineracy of

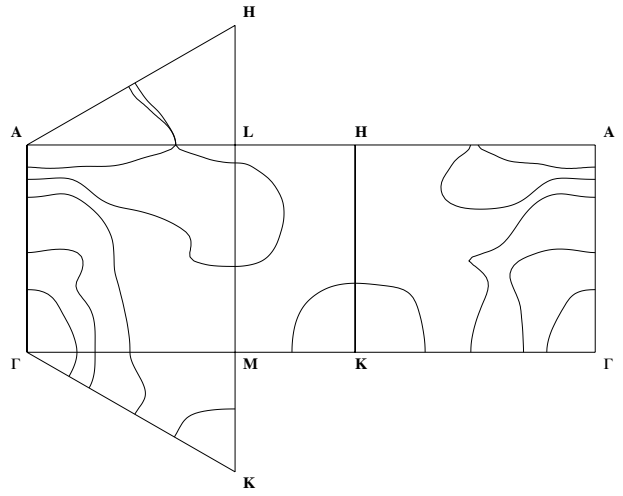

FIG. 5 Fermi surface of UPt_3 from local density band calculations (54), plotted in the high symmetry planes of the hexagonal Brillouin zone. This is composed of four electron surfaces - three around Γ and one around K - and two hole surfaces around A.

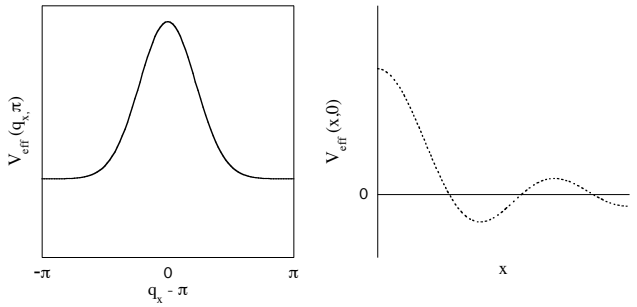

FIG. 6 Induced pair interaction from antiferromagnetic spin fluctuations (30). Momentum space (left) with a repulsive potential peaked at the magnetic wavevector Q. Fourier transform (right) showing Friedel-like oscillations, with a repulsive on-site potential, and an attractive potential for near-neighbor separations.

all the f electrons (56).

Given the resemblance to ^{3}He, it was not surprising that theorists tried to translate theories for ^{3}He over to the heavy fermion case. But trouble soon brewed. Neutron scattering measurements indicated the presence of antiferromagnetic spin fluctuations, *not* ferromagnetic spin fluctuations, in UPt_3 (57). Several groups then realized that this difference would lead to d-wave singlet pairing instead of p-wave triplet pairing (58; 59; 60; 61) (Fig. 6). In a single band simple cubic model, the pair state would be of the form $d_{x^2-y^2} \pm id_{3z^2-r^2}$. In real space, this corresponds to lobes that point from one atom to its six surrounding neighbors.

But there was the rub. UPt_3, even in a band theory description, is a very complex beast. Six j=5/2 f bands are in the vicinity of the Fermi energy (spin-orbit coupling being particularly strong). Of these, five are predicted to cross the Fermi energy. These bands are complicated admixtures of these f orbitals with uranium 6d and platinum 5d orbitals. Even constructing a pairing interaction at the phenomenological level is difficult, as two types of antiferromagnetic fluctuations are seen. The original 'high energy' ones correspond to antiferromagnetic correlations between near neighbor uranium ions (57). But after this, lower energy fluctuations were seen corresponding to antiferromagnetic correlations between next near neighbors (62). This frustrated interaction leads to stripe-like order, lowering the symmetry from hexagonal to orthorhombic. UPt_3 actually quasi-orders at this wavevector well above T_c, but with a tiny moment (that becomes large only when doped with other ions, like palladium). True long range order only sets in well below T_c (63).

Given these complications, what was done was to construct a model for the pair state based on experimental data. This led to surprising directions. First, UPt_3 does not exhibit any change in the Knight shift when going below T_c (64). This implies that the pair state is a triplet, certainly not what would naively expect based on antiferromagnetic fluctuations. Also, various measurements, such as thermal conductivity and transverse ultrasound, are most consistent with the presence of nodes (where the order parameter vanishes) on lines on the equator of the Fermi surface, along with 'quadratic' point nodes at the north and south poles where the gap varies quadratically with the polar angle (65; 66). In terms of spherical harmonics, the first one encountered with this property is Y_{32}. This is from the E_{2u} representation of hexagonal symmetry. It forms a 'triplet' state when multiplying this by $\hat{z}$. This acts to project the Cooper pair spins into the basal plane, consistent with the normal state spin susceptibility, and also the upper critical field, which indicates Pauli limiting (Zeeman pair breaking) for fields along the c axis (for in-plane fields, the Cooper pair spins can obviously align with the field direction). Note this 'triplet' is actually a 'singlet' when counting spin degrees of freedom. It is thought that the 'locking' of the d vector to the c axis is a consequence of the strong spin-orbit coupling in UPt_3.

There are a number of other advantages of this E_{2u} model (Fig. 7). Several years after the discovery of superconductivity in UPt_3, *two* superconducting phase transitions were discovered (67), again very reminiscent of ^{3}He. Then, it was realized that in a magnetic field, yet another transition takes place (68), making three superconducting phases altogether. Note that this last phase transition occurs for fields between the lower and upper critical fields associated with the vortex phase, and is thought to represent another distinct phase in the relative degrees of freedom (as opposed to a change in the vortex lattice, that would be associated with the center of mass degrees of freedom of the pair state). The resulting phase diagram in the H-T plane (Fig. 8) exhibits an unusual 'tetracritical' point where the three supercon-

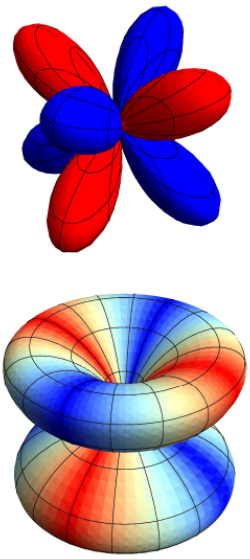

FIG. 7 E_{2u} (f-wave) order parameter (74). The bottom plot is Y_{32}, that is $k_z(k_x + ik_y)^2$. The top one is the real part of this.

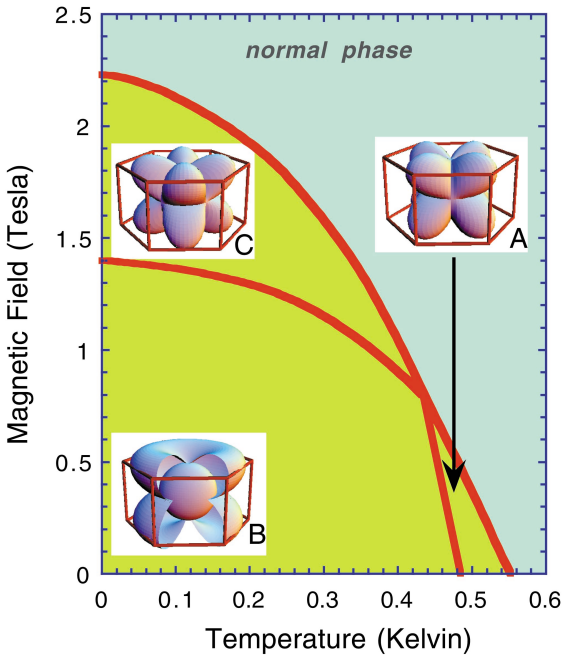

FIG. 8 Phase diagram of UPt_3 versus field (68), exhibiting three superconducting phases - A, B and C. In the E_{2u} model, the A phase would correspond to the top plot in Fig. 7, the B phase to the bottom one.

ducting phases and the normal phase touch.

There are two basic models that can explain these observations. First, two nearly degenerate solutions, ironically known as the A-B model (69) though for different reasons than ^{3}He. Here, A refers to one of the A single dimensional representations of the hexagonal group, and B to one of the B single dimensional representations. An advantage of this model is that it allows the tetracritical point to exist, since the A and B phase lines can cross since they come from different group representations, though the near degeneracy of the two solutions is an assumption with no real microscopic basis. The alternate model is for the order parameter to come from a two dimensional group representation, like E_{2u}. The advantage of this model is that it naturally explains the near degeneracy of the two zero field phase transitions. A likely source for the small degeneracy lifting is the small moment magnetism mentioned above, which leads to weak orthorhombicity. In support of this, under pressure, the double transition goes away at essentially the same pressure that the magnetism disappears (70). On the other hand, it is non-trivial for this model to account for the tetracritical point, since the various phases all originate from the same group representation, leading to level repulsion and thus an avoided crossing rather than a point of degeneracy. But this is a potential advantage of the E_{2u} model, in comparison to related models based on the d-wave E_{1g} (71) or p-wave E_{1u} (72) models. For the latter, the two bases of the two dimensional representation differ by two units of angular momentum (that is $Y_{2\pm1}$ for E_{1g}, and $Y_{1\pm1}$ or $Y_{3\pm1}$ for E_{1u}). The result is that gradient terms in the G-L free energy couple the two bases, leading to a splitting of the tetracritical point. On the other hand, the two partners in the E_{2u} case differ by four units of angular momentum ($Y_{3\pm2}$), and thus in an axial approximation, no splitting occurs. Hexagonal anisotropy will couple the two, but the hope is that this is weak, which is supported by explicit calculations (73). Strong support for the E_{2u} model has recently come from phase sensitive Josephson tunneling, which is consistent with a two dimensional representation with bases each having two units of angular momentum (74; 75). These measurements are also consistent with the predicted nodal structure of this state.

Still, a number of important questions remain. Both the phase sensitive tunneling and transverse ultrasound (76) indicate a single domain state, whereas any of the above two dimensional models would predict three different hexagonal domains. Why only one domain is realized in a macroscopic sample, and at that the 'right' one (the predicted transverse ultrasound only agrees with experiment for one of the the three domains (77)) is unknown. The d vector structure has also been brought into question (72), since the Knight shift indicates no change below T_c for any field orientation, which is most easily explained if the d vector can be rotated by the field. Even the nodal structure for E_{2u} has been recently questioned (78; 79). Still, if it is an f-wave E_{2u} state, there may be a relatively simple explanation for it. Plots of the spherical harmonics versus polar angle find that the maximum of the Y_{32} harmonic is close to the angle separating near neighbor uranium atoms in UPt_3 (Fig. 9). Therefore, if such a state is realized, it is in strong support of pairing models based on near neighbor interactions, such as

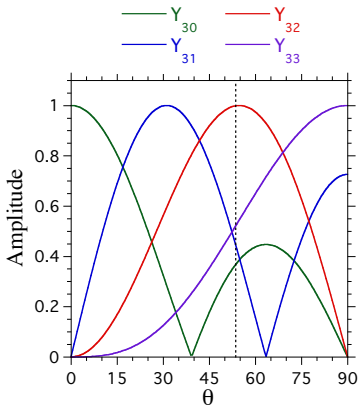

FIG. 9 Amplitude of Y_{3m} versus polar angle. The vertical dashed line is the angle corresponding to that of near neighbor uranium atoms in UPt_3, which is close to the maximum of Y_{32}.

occurs in models based on antiferromagnetic spin fluctuations. But then why a triplet in that case?

To understand this, we need to step back and look at the general problem of pairing in the presence of strong spin-orbit coupling, where spin is no longer a good quantum number. This was first addressed by Anderson (80). What he realized was that for a given state k, one can still define four degenerate states (assuming time reversal and inversion symmetries are not broken): k, Pk, Tk, PTk where P is the parity operator and T the time reversal one. From these four states (corresponding in the spin-only case to $k\uparrow, -k\uparrow, -k\downarrow, k\downarrow$) one can construct a 'singlet' and a 'triplet'. These states are respectively even parity and odd parity due to fermion anitsymmetry. This formalism has been exploited in great detail by a number of authors to understand the general structure of the order parameter (81). What one finds is that the same spin-orbit effects that were invoked above to lock the d vector to the lattice also act to mix in the other two d vector components (since spin is not a good quantum number). The requirement that all three components vanish can only occur on points on the Fermi surface, which is known as Blount's theorem (82). This would seem to eliminate any odd parity state description for UPt_3 if line nodes are indeed present, except there is an exception to the theorem. Pair states are classified by representations at the Γ point of the Brillouin zone since the center of mass momentum of the pairs is zero (though finite momentum pair states for UPt_3 have been advocated (83)). What this does not take into account, though, is the composite nature of such pairs. For non-symmorphic space groups (those with screw axes or glide planes), k states on the zone boundary have special properties. UPt_3 is an example, being a hexagonal close packed lattice with a screw axis. This leads to bands which stick in pairs on the zone face perpendicular to the c axis (84) (this phenomenon is responsible for the magnetic breakdown orbits seen in quantum oscillation measurements (53; 54)). The same phenomenon causes all three d vector components to vanish on the zone face for certain odd parity representations (85; 86). Therefore, those Fermi surfaces which cross the zone boundary can indeed have line nodes for a general pair state involving all three d vector components. Interestingly, these general pair states bear little resemblance to the spherical harmonics mentioned above (87; 88), and therefore one should view with caution statements that material X has 'p', 'd', or 'f' wave pairing.

Much time has been spent discussing the UPt_3 case since it is an illustrative example of what is involved when discussing a complex multi-band material in the presence of strong spin-orbit coupling. But there are many other examples of heavy fermion superconductors which reveal a great wealth of phenomena. UBe_{13} was discovered at about the same time as UPt_3, but it seems to be a very different animal. Unlike UPt_3, where Fermi liquid like behavior sets in well above T_c, in UBe_{13} it never sets in (51). That is, the superconductor emerges from a non-Fermi liquid normal state. This is profound, since superconductivity is an instability of the normal state, and the underlying supposition of BCS is that the normal state is composed of quasiparticles. Little is known about the superconducting state, though it appears that again, there are multiple superconducting phases (this particularly becomes evident when one dopes with thorium (89)).

At about the same time as the materials discussed above, superconductivity was discovered in URu_2Si_2 (90). This material continues to be fascinating because of the unknown nature of its normal state. At 17K, a transition occurs to what was thought at the time to be an antiferromagnetic state. Yet subsequent neutron scattering measurements found the ordered moment to be tiny (91), far too small to explain the large specific heat anomaly that indicates that most of the Fermi surface has been removed. After many years, it was realized that internal strain was responsible for the small moments, and therefore the 'hidden order' phase is not magnetic, though it appears to be related to an antiferromagnetic phase, which can be induced by either doping or pressure. What it is still remains a point of great speculation (92), and until this is resolved, the nature of the superconducting state will be difficult to resolve as well. One of the most intriguing suggestions is that the hidden order is due to some higher multipolar order (93; 94; 95), though to date, no evidence of this has been forthcoming from x-ray measurements.

There are, though, close cousins which exhibit robust antiferromagnetic order: UPd_2Al_3 and UNi_2Al_3 (96). That is, the superconducting state emerges from an antiferromagnet. Knight shift measurements are consistent with a 'singlet' for the former but a 'triplet' for the latter (97). Although the presence of antiferromagnetism does break time reversal symmetry, singlet pairing is still possible - the actual order parameter being a linear combination of a spin singlet with zero center of mass momentum

and one component of a spin triplet with a momentum equal to the antiferromagnetic wavevector (98). UPd_2Al_3 was the first heavy fermion superconductor to exhibit a spin 'resonance' as seen by inelastic neutron scattering. ^{3}He has many collective modes of the superconducting order parameter (99), but this is due to strong degeneracy of the order parameter (three orbital times three spin degrees of freedom) and its neutral nature. In conventional charged superconductors, collective modes have not been found, except for the Carlson-Goldman mode (100) (a 'phase' mode which occurs near T_c because of backflow of the normal carriers (101)), the Higgs mode (102) (which only becomes a true collective mode when it is pulled below the 2Δ continuum due to interactions, as occurs when superconducting and charge density wave order coexist (103; 104)), and the 'Leggett' mode (105) (where the relative phase of the order parameter of a multi-band system can oscillate, as thought to have been seen by Raman scattering in MgB_2 (106)).

The suppression of collective modes can be understood from the BCS coherence factors. The polarization bubble in the superconducting phase is composed of two terms: GG and FF, where G is the normal and F the anomalous (Gor'kov) Green's function. Typically, these two contributions cancel on the mass shell, leading for instance in the s-wave case to a square root growth in frequency of the conductivity above the 2Δ threshold (the 'missing' weight shows up as the condensate peak at zero frequency). But if the order parameter should change sign under translation by a given Q vector, then in the resulting finite momentum response, GG and FF reinforce one another rather than cancel since the sign of FF flips. This leads to a step jump in the imaginary part of the bubble at $\hbar\omega_{th} = \min_k(|\Delta_k| + |\Delta_{k+Q}|)$, which by the Kramers-Kronig relation leads to a log divergence in the real part. This divergence causes a pole to be pulled below the continuum within a linear response (RPA) treatment where $\chi = \chi_0/(1 - I\chi_0)$ with χ_0 the bubble and I the exchange interaction in the case of the dynamic spin susceptibility. Thus, the observation of a spin resonance in UPd_2Al_3 at the antiferromagnetic wavevector implies the existence of such an order parameter (107), though alternate possibilities have been suggested (magnons associated with the ordered magnetic phase become less damped below 2Δ (108)).

The question of whether magnetic correlations are responsible for heavy fermion superconductivity provided a guiding principle when looking for new ones. In a classic paper (109), Gil Lonzarich's group demonstrated that the antiferromagnetic phases in $CeIn_3$ and $CePd_2Si_2$ were suppressed with pressure. At the 'quantum critical' point where the order was suppressed to zero, a 'dome' of superconductivity appeared (Fig. 10). This implied that quantum critical fluctuations associated with the magnetic order might potentially be the pairing 'glue'. Interestingly, this physics is similar to that proposed by Levin and Valls for ^{3}He (40), yet in this case, the maximum T_c appeared to be *at* the critical point rather than displaced

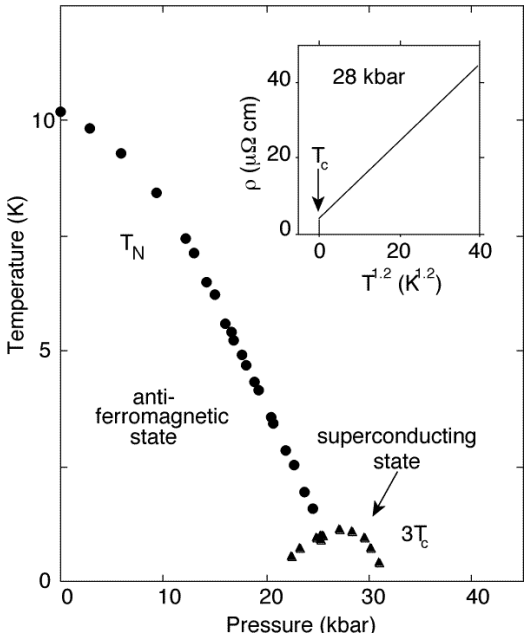

FIG. 10 Phase diagram of $CePd_2Si_2$ versus pressure (109). The inset shows the resistivity at 28 kbar, which is quasilinear in T.

to the paramagnetic side as they predicted.

The discovery of Mathur *et al.* promoted a resurgence in the field of heavy fermion superconductivity. A few years later, superconductivity was discovered in the $CeXIn_5$ compounds (110), where X is a transition metal (Co, Ir, Rh). These materials are layered analogues of cubic $CeIn_3$, and show superconducting phases overlapping with antiferromagnetic phases (Fig. 11). Recently, the superconductivity was seen to persist to just a few layers (111). Perhaps more dramatically, a plutonium analogue was found to superconduct at 18.5 K (112). This T_c was almost an order of magnitude larger than any previously known heavy fermion superconductor. NMR measurements for all of these materials indicate 'singlet' pairing, and evidence for order parameter nodes have been provided by a variety of measurements. Therefore, in the literature, these have been referred to as 'd' wave superconductors, with the caveat that the notation may be somewhat misleading because of the multi-band nature of these materials along with strong spin-orbit coupling. One of the more intriguing aspects is a new phase that appears at low temperatures just below the upper critical field in $CeCoIn_5$ (113). In the beginning, it was felt this might be the long predicted 'LOFF' state (where the electrons pair at finite momentum to help offset the deleterious effects of the Zeeman splitting on the pairs), but recent neutron data point instead to a novel magnetic phase that is only stable below the upper critical field (114).

The other unusual discovery was that of superconductivity in UGe_2 (116) and URhGe (117). These materials are *ferromagnetic*. Moreover, the superconducting

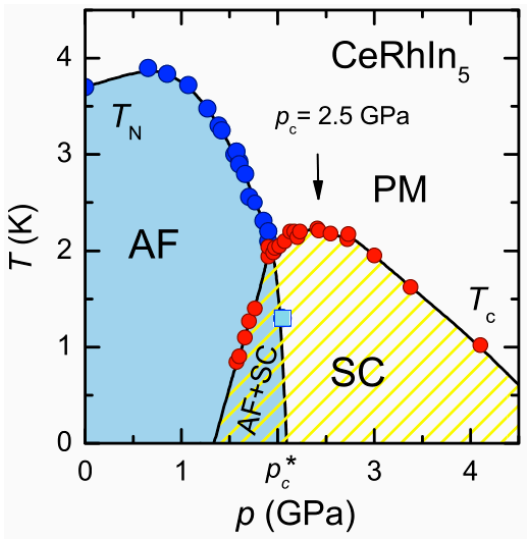

FIG. 11 Phase diagram of $CeRhIn_5$ versus pressure (115). Note the coexistence region of antiferromagnetism and superconductivity.

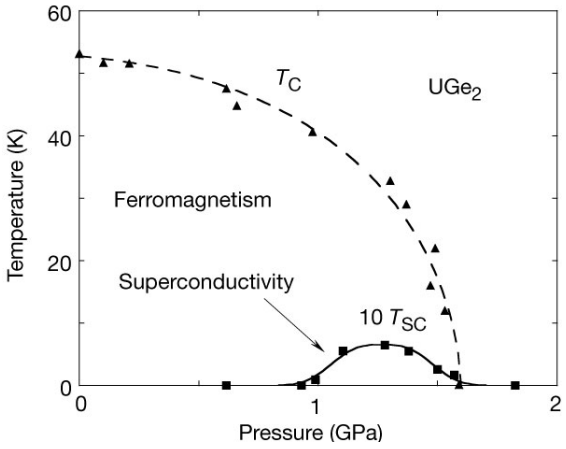

FIG. 12 Phase diagram of UGe_2 versus pressure (116). The superconducting dome is completely inside the ferromagnetic phase.

'dome' (T_c versus pressure) in UGe_2 is enclosed entirely within the ferromagnetic phase (Fig. 12). URhGe exhibits an unusual 'reentrant' behavior where upon applying a magnetic field, superconductivity is suppressed, then reappears at a higher field (118). Obviously, the pair state in these materials is thought to be a 'triplet', but little is known about its properties (119).

We now turn to microscopics. Heavy fermion behavior typically occurs near the borderline between localized and itinerant behavior for the f electrons, the so-called Hill limit (120). Rare earth impurities in transition metals are well known to exhibit the Kondo effect, where scattering of the conduction electrons off the f ions leads to a logarithmic divergence of the resistivity as the temperature is lowered (121). This is a good example of where perturbation theory breaks down in an unusual way (it is third order in the interaction before the log shows up). The Kondo problem was first solved by Ken Wilson in 1975 using the numerical renormalization group (122), where below the so-called Kondo temperature, the conduction electrons bind to the f electrons to form singlets, reminiscent of BCS theory. This can presumably be extended to a dense array of such local ions, forming a 'Kondo lattice'. Realistic treatments of the problem are based on the Anderson model (123), which allows the f occupation to be non-integer and thus accounts for f charge fluctuations - the Kondo limit being the limit that the f occupation goes to an integer value (i.e., the Coulomb repulsion U goes to infinity), and thus only f spin fluctuations remain. The solution of this problem can be seen as a local f level which interacts with the conduction band, forming two 'hybridized' bands (this is a correlated analogue of band theory). If the chemical potential falls inside the gap (integer occupation of f and conduction), one has a 'Kondo insulator' (currently the rage because it is a potential topological insulator with conducting surface states (124; 125)). If just outside the gap, one has a very heavy mass.

One can go beyond this mean field treatment by the use of slave bosons with a gauge field that incorporates the constraint of near integer occupation of the f electron (with the scalar part of the gauge field related to the f charge, and the vector part related to the f current) (126). In this case, a perturbation expansion is possible in $1/N$, where N is the degeneracy of the f orbitals. N is six for the j=5/2 orbitals appropriate for cerium, but obviously in the low energy limit, N typically reduces to 2 because of crystal field splitting of the f levels. The principal fluctuations beyond mean field theory are hybridization fluctuations. By considering the anomalous self-energy, these 'Kondo bosons' can intermediate higher angular momentum pairing (127). One disadvantage of this approach is that spin fluctuations do not show up until order $1/N^2$ (128). This can be cured by going to a spin rotationally invariant formalism.

Since these early days, many theories for heavy fermion superconductivity have been proposed, ranging from the paramagnon and 'Kondo boson' approaches mentioned above, to phonons and valence fluctuations. That phonons could play some role is evident from the very large Gruneisen parameters observed in heavy fermion metals. That valence fluctuations can play some role is evident from the phase diagram of $CeCu_2Si_2$ (Fig. 13). The pressure dependence of T_c is complicated, but upon doping with germanium (which suppresses T_c), it was seen that the superconducting 'dome' was actually composed of two domes (129). The first (smaller) one is associated with a quantum critical point where magnetic order disappears similar to $CeIn_3$, but the second (larger) one appears to be associated with a valence change of the f electrons.

Reviewing the full breadth of these theories would take its own review article. Suffice it to say that as of yet,

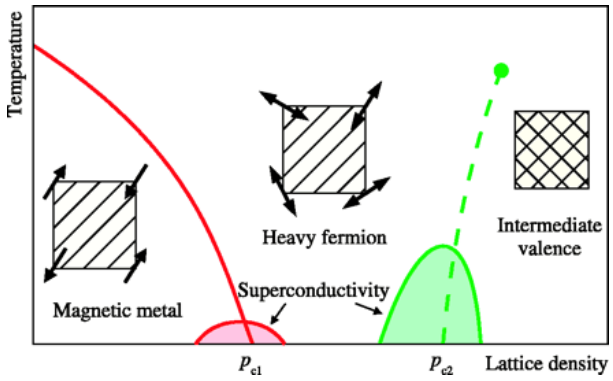

FIG. 13 Schematic phase diagram of $CeCu_2Si_{2-x}Ge_x$ versus pressure (129). Two superconducting domes are present, the left one associated with a quantum critical magnetic point, the second with a volume collapse transition.

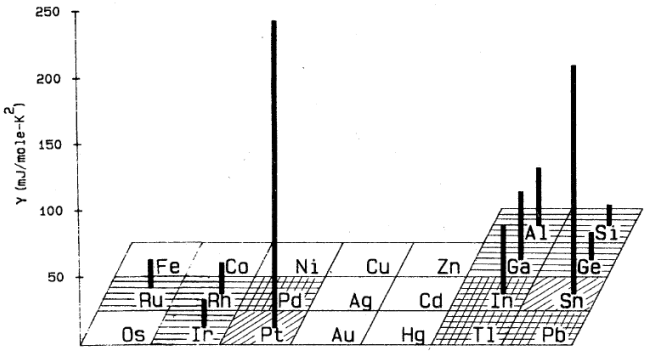

FIG. 14 Low temperature specific heat coefficient for various UX_3 alloys (130). All have the cubic $AuCu_3$ structure except for quadrupolar ordered UPd_3 (double hexagonal close packed) and superconducting UPt_3 (hexagonal close packed).

there is no predictive theory that has emerged - some heavy fermion systems are magnetic (some of those even exhibiting itinerant spin density wave behavior), some are superconducting, and some are 'vegetables', and we have little feeling for why this is so. What is known is that heavy fermion superconductivity seems to occur under special conditions. For instance, Fig. 14 shows the UX_3 materials (130). Almost all of them have the cubic $AuCu_3$ structure, and exhibit a wide range of behavior, but none of them are superconducting. The exception structure wise is UPd_3 (double hexagonal close packed) which exhibits quadupolar order of localized f electrons, the other is superconducting UPt_3 (hexagonal close packed). Why certain crystal structures seem to be amendable to superconductivity is not known - for instance, $CeCu_2Si_2$ and URu_2Si_2 both have the $ThCr_2Si_2$ structure, as does $BaFe_2As_2$ (which becomes a high temperature superconductor upon doping as will be discussed below).

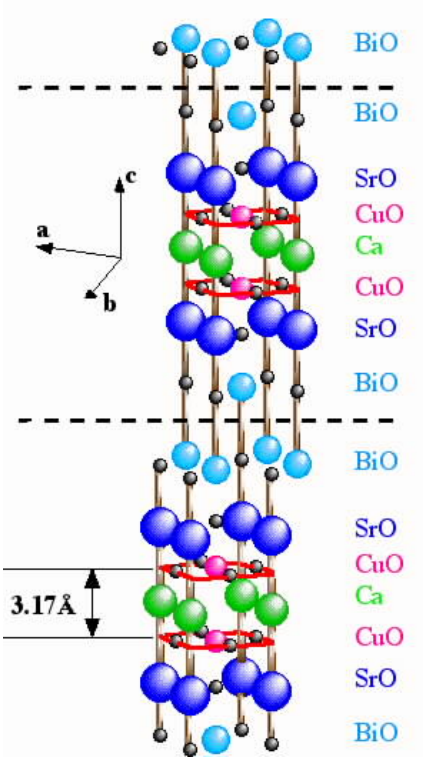

FIG. 15 Crystal structure of the cuprate Bi2212. Bilayers of CuO_2 units are separated by insulating spacer layers of SrO and BiO. The dashed lines indicate a well defined cleavage plane, making this material ideal for ARPES and STM studies. Figure courtesy of Adam Kaminski.

IV. CUPRATES

V_3Si was discovered in 1953 (131), and this class of A15 cubic materials had the highest known T_c (23 K for Nb_3Ge) until the cuprates were discovered in 1986 (132). This long stretch of time was what led to theoretical speculations that this might be the highest one might ever get to (17). In fact, in the beginning, few people paid attention to the Bednorz-Muller paper on Ba doped La_2CuO_4 since in the past, there had been so many sightings of 'superconductors' which had turned out to be false (so-called USOs - unidentified superconducting objects). But about six months after their discovery, their finding was verified by Tanaka's group, and progress became rapid, with the identification of superconductivity above liquid nitrogen temperature a few months later in the related material $YBa_2Cu_3O_7$ (133). Since then, several classes of these materials have been discovered (Fig. 15), with one variant having a T_c (under pressure) of 164 K (134).

The discovery of the cuprates was a tremendous surprise. It violated most of Matthias' rules, as it was a quasi-2D doped insulating oxide. But the discoverers were not searching blindly. Low temperature superconductivity had been seen many years before in the doped perovskite $SrTiO_3$ at ridiculously low carrier concentra-

tions (135). Bednorz and Muller's guiding principle was to look at other oxides where Jahn-Teller distortions played a crucial role (136). The cuprates were a prime example, where such distortions lead to a half-filled $d_{x^2-y^2}$ level, copper being in a d^9 configuration. This guidance was based on the idea that such strong lattice distortions could lead to strong coupling electron-phonon pairing via bipolaron formation (137).

But this bipolaron picture has turned out to be the minority view. In fact, the community working on heavy fermions rapidly turned their attention to the cuprates in 1987. Simply reducing the dimensionality from three to two (a square lattice network) in theories based on antiferromagnetic spin fluctuations led to the early prediction of $d_{x^2-y^2}$ pairing (138) (Fig. 6). Further support for this theory came out at about the same time when neutron scattering revealed that the undoped parent insulating phase was a commensurate antiferromagnet with $Q = (\pi, \pi)$ (139). In the beginning, there was a lot of resistance to such a non s-wave state, given the high T_c and seeming insensitivity to disorder, but based on the d-wave prediction, evidence begin to emerge that order parameter nodes were indeed present - penetration depth measurements indicated a linear in T penetration depth at low temperatures (140) and angle resolved photoemission was consistent with a node along the zone diagonal as expected for such a d-wave state (141). Definitive evidence came when phase sensitive Josephson tunneling was able to detect the sign change in the order parameter upon ninety degree rotation (142), at which point all but a few skeptics were convinced.

One might have thought this would settle the debate, but such was far from the case. In the same month that the discovery of YBCO was announced, Phil Anderson proposed an alternative picture (143). Anderson early on had realized certain crucial aspects of the cuprate problem - low dimensionality, quantum limit of the spins (the single d hole has a spin of 1/2), and the nature of the insulating state (Fig. 16). For a half filled band, band theory predicts metallic behavior, but in the presence of a large Coulomb repulsion, U, the electrons would localize, forming a Mott insulating state with an energy gap between a lower Hubbard band and an upper Hubbard band. Band theory can simulate this by mapping one band to an 'up' spin state, and the other to a 'down' spin state, but Anderson felt these arguments were fallacious, since they equated the exchange interaction with the on-site U. In fact, he felt that the Mott phenomenon was independent of whether the ground state was magnetic or not, and the theory he proposed was based on an earlier paper seeking to understand the nature of frustrated magnetism (144).

To understand this, note that in the Mott case, magnetism is induced by the superexchange interaction (145). In essence, if the spins are aligned between near neighbors, there is no gain in the free energy by the Pauli exclusion principle, but if they are anti-aligned, one can gain energy by virtual hopping. By second order perturbation theory, this energy is $4t^2/U$ where t is the hopping integral, defining the superexchange J. Now consider a Néel lattice. The exchange energy for a given site is zJ where z is the number of neighbors. On the other hand, consider singlet formation for $S = 1/2$ spins. The exchange energy per singlet is $3J$. For a square lattice, $z = 4$, so the Néel state wins. But allow the singlets to fluctuate from bond to bond. Anderson speculated that the resulting free energy gain might be sufficient to tip the balance in favor of a liquid of spin singlets rather than a Néel lattice (Fig. 17), hence the term 'resonating valence bonds' (RVB). Although Anderson was wrong in that the undoped material does form a Néel lattice (but with a moment reduced to 2/3 its classical value), it was later found that for hole doped materials, only a few percent of holes is sufficient to destroy magnetism, indicating that the basic idea might be right.

The RVB theory has been controversial to say the least. One well known physicist quipped that the initials actu-

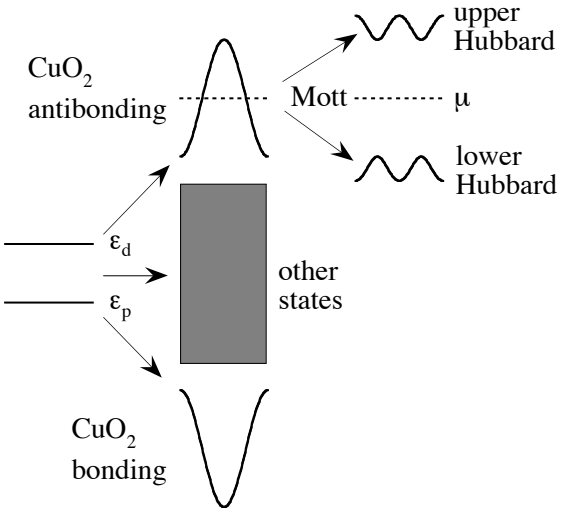

FIG. 16 Basic electronic structure of the cuprates. Copper $d_{x^2-y^2}$ orbitals hybridize with planar oxygen p_x and p_y orbitals, forming bonding and antibonding combinations. Correlations cause the half filled antibonding band to split into lower and upper Hubbard bands.

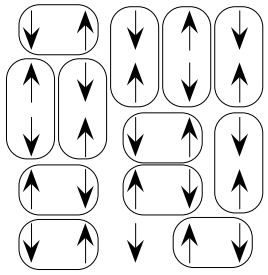

FIG. 17 An RVB state is a liquid of spin singlets, with unpaired spins denoted as spinons.

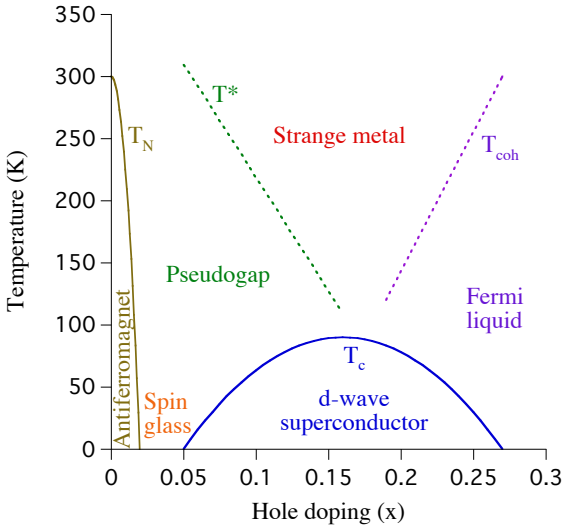

FIG. 18 Phase diagram of cuprates versus hole doping. Three normal phases surround the superconducting dome: the pseudogap phase, and two gapless phases - a strange metal exhibiting a linear T resistance, and a more conventional Fermi liquid.

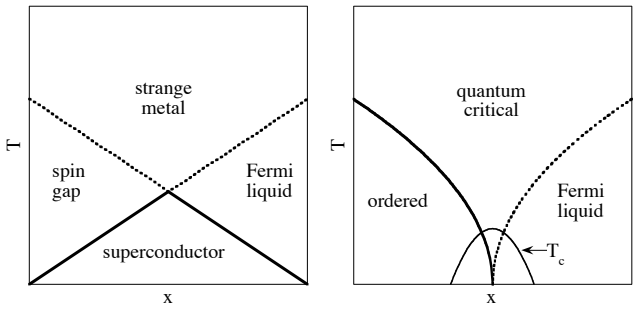

FIG. 19 Two proposed phase diagrams of the cuprates - RVB (149) (left) and quantum critical (150) (right).

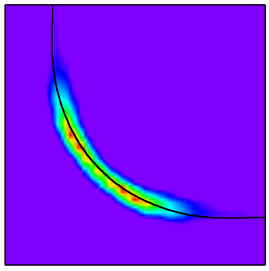

FIG. 20 Zero energy intensity from photoemission for the cuprate Bi2212 in the pseudogap phase, exhibiting an arc of gapless excitations (159). The large Fermi surface in the gapless normal phase is shown as the black curve.

ally stood for 'rather vague bullshit'. Another wrote an extended poem (based on Hiawatha!) claiming Anderson was leading young physicists down the primrose path, supposedly to their ultimate destruction (146). Still, its profound influence in the field cannot be denied.

Anderson's original theory was the so-called 'uniform' RVB state. In such a theory, free S=1/2 degrees of freedom ('spinons') form a Fermi surface. But shortly afterwards, it was realized that upon doping with carriers ('holons'), the lowest energy ground state was equivalent to a d-wave liquid of spin singlets (147). In fact, RVB theory gave one of the first predictions of the temperature-doping phase diagram of the cuprates (Fig. 18), with four regions identified (Fig. 19a). Below a temperature T^* that decreases linearly with the doping, the d-wave spin liquid would form, leading to a d-wave energy gap in the spin excitation spectrum. Below a temperature T_{coh} that increases linearly with the doping, the charge degrees of freedom would become phase coherent, leading to Fermi liquid behavior. Below both temperatures, the combination of a d-wave spin singlet with charge coherence would give rise to a d-wave superconductor, which thus forms a 'dome' in the temperature-doping phase plane. Above both temperatures, one would have instead a 'strange metal' phase, exhibiting gapless non Fermi liquid behavior. There are some photoemission data which are in support of this picture for the phase diagram (148).

These ideas were emerging at about the same time as NMR experiments were revealing the presence of a 'spin gap' that roughly had the doping dependence indicated by the RVB theory (151). Subsequently, this 'pseudogap' was revealed by a number of other probes, including c-axis infrared conductivity (152), photoemission (153; 154; 155) and tunneling (156). Its observation by angle resolved photoemission (ARPES) was particularly illuminating, in that the inferred gap appeared to be d-wave like in nature. How d-wave like is a matter of continuing debate. What is clear is that the Fermi surface is truncated in the pseudogap phase into 'arcs' centered at the nodes of the d-wave superconducting state (157; 158) (Fig. 20). What is not clear yet is whether these arcs represent one side of a closed pocket in momentum space (153) or a thermally broadened d-wave node (159). The latter is consistent with RVB theory, and further evidence has been given by its consistency with some low temperature photoemission data for non superconducting samples (160) which continue to exhibit a d-wave like gap. But increasing attention has been given to the former possibility.

If some kind of order were present in the pseudogap phase, a reconstruction of the Fermi surface into smaller pockets would be expected. For instance, simple Néel antiferromagnetism in the doped case would initially give rise to a small hole pocket centered around the $(\pi/2, \pi/2)$ points (161). In the early days of cuprates, such a possibility was actively discussed, and was implied as well in the initial ARPES study of Marshall *et al.* (153). The idea here is that the transition to long range magnetic order is determined by coupling between the CuO_2 planes, since Heisenberg spins in two dimensions do not order. As mentioned above, a few percent of doped holes is suf-

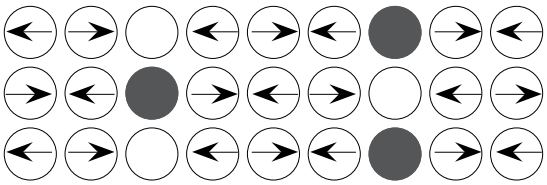

FIG. 21 A schematic for stripes, where doped holes (dark circles) form ribbons of charge separated by undoped antiferromagnetic regions (167).

ficient to disrupt this order. Still, fluctuating two dimensional order is likely still present, and if the fluctuations are slow enough, an apparent pocket might be formed (162). The resulting 'shadow' bands were subsequently seen by several ARPES studies (163), but in all cases we know, they appear to actually be due to the crystal structure - Bi2201, Bi2212, and LSCO have (π, π) as a reciprocal lattice vector due to orthorhombic distortion of the crystal lattice.

This picture, though, got further support when quantum oscillation data finally emerged. In the early days of cuprates, such studies were done, but led to inconclusive results. But with the advent of high quality crystals, the first definitive data appeared in 2007 (164). These initial experiments were done on underdoped YBCO (the so-called ortho-II phase with a well ordered crystal structure). What they revealed was a small pocket, first seen by quantum oscillations of the Hall resistance. But interestingly, the Hall resistance was negative, indicating that the pocket was an electron pocket, despite the fact that one is hole doping (165). This led to the speculation that such pockets could arise from incommensurate order due to the formation of magnetic stripes (166).

Such magnetic stripes were first identified by neutron scattering (167) (Fig. 21). They are particularly pronounced near 1/8 doping. There are two ways one might think of such stripes. First, as an incommensurate spin density wave state, similar to chromium. Here, the incommensurability is due to doping, which moves the chemical potential away from half filling for the hybridized copper-oxide band. The other picture is a real space one - doped holes do not go in homogeneously, but in order to minimize their Coulomb repulsion, form rivers of charge (168; 169). In between these rivers of charge are undoped antiferromagnetic regions. Therefore, the 'incommensurability' in this case is due to a phase slip of the simple Néel lattice when moving across the stripes. The lack of observation of higher harmonics in the neutron data seemed to suggest the former, but spectacular scanning tunneling data seem most consistent with the real space picture (170). The fact that quantum oscillation data and the region of negative Hall effect seem to form a dome around 1/8 doping definitely point to stripes as the origin of the pockets (171).

The remaining question has concerned charge versus magnetic stripes. In 1/8 doped LBCO (one of the few materials where static stripe order is observed), charge ordering occurs before spin ordering (172). Charge ordering as an explanation of the quantum oscillation results had been discounted because of difficulties in getting an electron pocket in that case (166), but it was subsequently shown that a nematic distortion (where x-y degeneracy is broken) was sufficient to stabilize them (173). In fact, one generally expects that as one reduces the temperature, nematicity appears first, followed by charge order and then eventually by spin order (170; 174). Interestingly, data on the Nernst effect in YBCO are consistent with nematicity setting in at the pseudogap temperature, T^* (175). But the problem with these scenarios is that the electron pocket is in the $(\pi, 0)$ region of the Brillouin zone, exactly where ARPES sees a large pseudogap.

Because of this, an alternate picture has emerged (176). Here, the Fermi arcs instead of closing towards the $(\pi/2, \pi/2)$ points (which would form hole pockets) instead close towards the $(0, 0)$ point (to form electron pockets). The translation of the arcs to form such a pocket is achieved by having biaxial charge order. Recently, such order has indeed been seen by x-ray studies (177; 178). So, this would seem to settle matters, except for the fact that no evidence for a closed pocket near the $(0, 0)$ point of the Brillouin zone has ever been inferred from photoemission data.

To complicate matters, another type of novel magnetic order has been seen to set in at T^* (179). The origin of this finding goes back to the early days of cuprates when it was realized that in the 'strange metal' phase, the resistivity was linear in temperature (180). Although at high temperatures this is not a surprise (the electron-phonon interaction can cause this), at lower temperatures this was a puzzle, particularly since it was observed in samples of Bi2201 where T_c was very low. Although various models have been suggested to account for this linearity, the most straightforward one was proposed by Varma and collaborators in 1989 (181). If one has a bosonic spectrum that is flat in energy (ω), then the imaginary part of the fermion self-energy due to interaction with those bosons will be linear in ω. If one assumes a momentum independent interaction, then this translates to a linear T resistivity. This has been denoted as marginal Fermi liquid theory. The experimental motivation for this conjecture was the roughly frequency independent background observed in Raman scattering. Further support for this conjecture was found when a linear ω behavior of the imaginary part of the self-energy was identified by ARPES (182). A subsequent ARPES study was consistent with this linear ω term being roughly momentum independent (183).

Later, Varma proposed a microscopic theory along these lines (184). His conjecture was that the single band Hubbard model, which was the theoretical underpinning for most theories, was an inadequate model for the cuprates. In particular, because of the hybridization between the copper $d_{x^2-y^2}$ orbital and the oxygen p_x and

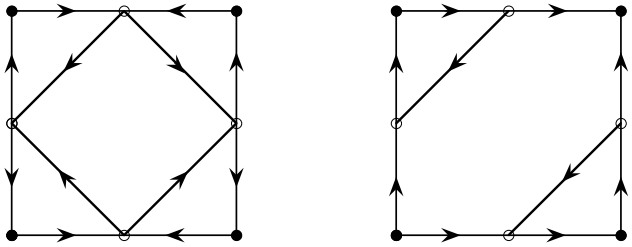

FIG. 22 Two orbital current patterns proposed by Varma (188). Filled circles are copper, empty circles oxygen. The right pattern is consistent with photoemission (186) and neutron scattering (179) data.

p_y orbitals, he felt that a three band model was a minimal description. In the process of studying such a model, he found a new ground state where currents flowed inside the CuO_2 network of ions. Although flux states had been proposed before (they occur in RVB models), this flux state was unique in that it did not break translational symmetry (Fig. 22). In essence, it is an orbital antiferromagnet with $Q = 0$ (allowed since there are two oxygens in the square lattice unit cell). An initial neutron scattering study did not find this state (185), but a subsequent ARPES study using circularly polarized light potentially identified it via dichroism (186). This identification, though, required a rotation of the originally predicted current pattern by 45° (an alternate ground state that Varma had not initially considered). Once this was realized, neutron scattering indeed identified the state in underdoped YBCO (179). Subsequent studies have found this state in Hg2201, Bi2212, and a short range ordered version in LSCO (187).

The observed moment is substantial, up to a few tenths of a μ_B per CuO_2 unit. But it has not been observed by either NMR or μSR measurements (189). This has led to some skepticism that the effect could be an artifact - structural transitions can lead to a change in the spin flip ratio in neutron scattering, and such a structural effect could explain the ARPES dichroism results as well. If it were some novel structural transition, though, it has yet to be identified, though there is a claim of seeing inversion breaking from x-ray natural dichroism (190), which would also be consistent with recent STM results where a difference is seen between the two oxygen sites (191). Whatever it is, it does have an order parameter like evolution that sets in at T^*, which confirms Varma's original conjecture that the pseudogap phase represents some sort of symmetry breaking.

Subsequent work by Kapitulnik's group identified an optical Kerr rotation that sets in below the T^* line identified by neutron scattering in YBCO (192), but appears to be coincident with it in Bi2201 (193). It now appears that the Kerr signal is coincident with the biaxial charge order recently identified in underdoped YBCO (177; 178). This has led to speculation that the Kerr signal might be due to some kind of 'chiral' charge density wave that breaks inversion symmetry (194) (in Bi2201, the crystal space group already breaks inversion symmetry). Alternately, the Kerr signal could simply be a signature of a magneto-electric phase, as occurs in antiferromagnetic Cr_2O_3 (195) or in an orbital current phase with a structural distortion as Varma suggests (196). Whether these various symmetry breakings can explain a large pseudogap remains to be seen. Certainly, the T dependence of the pseudogap identified by ARPES follows that of the Kerr signal in Bi2201 (193). But nematics, which orbital currents are related to, do not necessarily generate an energy gap, and it is also doubtful whether the weak charge order identified by x-ray scattering could cause a large energy gap. Stripe models, on the other hand, do generate a gap, with the spin gap in the undoped regions between the stripes inducing a gap in the mobile holes from virtual hopping of the holes into these regions (197). Virtual hopping of pairs of mobile holes into these undoped regions is also a potential source for the superconductivity (197).

One reason for highlighting all of these results (nematics, stripes, orbital currents, etc.) is not only to emphasize the complexity of the pseudogap phase, but that such results highlight the strong possibility of an alternative phase diagram to the RVB one, where an ordered phase is suppressed to zero by doping, ending at a quantum critical point (Fig. 19b). The T_{coh} phase line would then be the 'quantum disordered' mirror of the T^* line. Above these two lines, quantum criticality would occur, which would then explain the non-Fermi liquid behavior of the 'strange metal' phase. More importantly, if we make an analogy to the previous section on heavy fermions, one might suspect that the fluctuations in the quantum critical regime associated with the pseudogap phase would be the origin of the pairing in the superconducting phase. Regardless, since superconductivity is an instability of the normal phase, and the fact that over much of the phase diagram, superconductivity occurs below the T^* line, a proper identification of the nature of the pseudogap phase will be critical for the ultimate theory of cuprates (198).

Superconductivity also occurs in electron doped cuprates (199) (Fig. 23). Here, commensurate antiferromagnetism occurs over a much larger range of doping than in the hole-doped case, with the pseudogap phase associated with this magnetism (in the 2D limit, one expects a pseudogap phase in the renormalized classical regime above the magnetic ordering temperature (200)). Many of the properties of the electron doped side are similar to the hole doped one (d-wave superconductivity, pseudogap, non Fermi liquid behavior), suggesting that the origin of superconductivity is the same. If so, this is definite support for those theories which suggest that magnetic correlations are responsible for the pairing, as thought to be the case in heavy fermions. Although it was originally felt that magnetic correlations weaken significantly with doping, recent resonant inelastic x-ray (RIXS) studies on YBCO (201) and Bi2212 (202) indicate

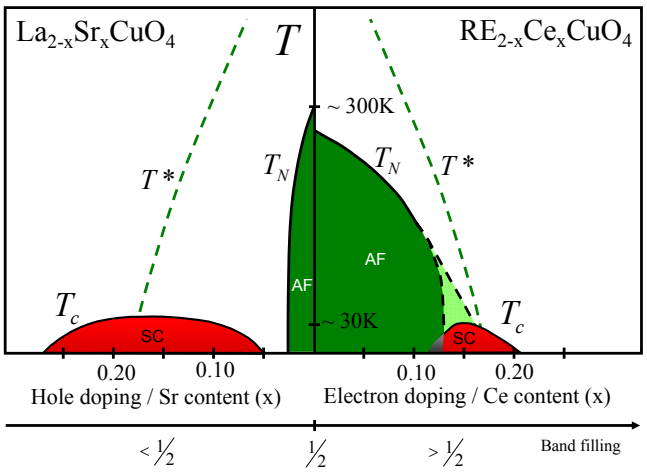

FIG. 23 Combined electron and hole doped phase diagram of the cuprates (199). Note that the antiferromagnetic phase extends over a larger doping range in the electron doped case.

that strong spin fluctuations are still present at optimal doping.

The various theories discussed above have led to a passionate debate on the nature of the pairing in cuprates. In antiferromagnetic spin fluctuation theories, pairing is treated in an approximation similar to the electron-phonon case - that is, by virtual exchange of spin fluctuations (58; 59; 60; 61). The pairing interaction is proportional to the dynamic spin susceptibility, and thus the source of pairing is an induced interaction that is confined to energies of order 0.4 eV or less. This is in contrast to RVB theories, where the pairing is encoded in the 'normal state' wavefunction, and the interaction is associated with the superexchange J which should only develop dynamics on an energy scale of order U (203). Dynamical mean field theory calculations in the cluster approximation are in support of the former picture (204) even though such calculations do exhibit RVB like behavior, with singlet formation particularly pronounced for four site copper plaquettes (205). Certainly, changes in the optical response of cuprates below T_c have been observed up to 5 eV (206) indicating that the effects of pairing extend over a large energy range. This may be related to other optics experiments (207) that indicate a lowering of the kinetic energy below T_c in underdoped materials, where the resulting increase in low energy spectral weight would come at the expense of high energy spectral weight (coming from an energy scale of U). This is very different from the increase of the kinetic energy that occurs in BCS theory due to particle-hole mixing. In essence, the potential energy decreases when the energy gap is formed in the pseudogap phase, but the electrons remain incoherent. Only below T_c does coherence occur, leading to a decrease in the kinetic energy. This has been suggested to be in support of pre-formed pairs in the pseudogap phase (as also implied by the large Nernst signal in the pseudogap phase (208)), but kinetic energy lowering has been seen as well in dynamical mean field calculations where the existence of pairing above T_c has not been identified (209).

Given the diverse nature of the phenomena in cuprates, it has been difficult to come up with a 'smoking gun' for pairing. Attempts to extract the anomalous self-energy from planar tunneling, ARPES, and scanning tunneling probes have been inconclusive up to now, mainly because of the strong momentum dependence associated with d-wave pairing, along with the complications of a normal state pseudogap, though looking at the angle resolved density of states instead can help (210). Attempts to analyze the 'normal state' self-energy indicate the presence of spin fluctuations (211; 212), phonons (213), and a frequency independent bosonic background similar to what is seen in Raman scattering (214; 215). Much focus has been put on the 'spin' resonance below T_c, which was first identified in cuprates (216) before being seen in several heavy fermion superconductors (and later in pnictides). Although this could simply be consistent with having d-wave pairing (the d-wave state reverses sign under translation by $Q = (\pi, \pi)$), neutron scattering does indicate that the formation of the resonance is associated with a lowering of the overall exchange energy below T_c (217), though it should be remarked that because of phonon contamination in the data, uniquely extracting the spin fluctuations over a large range of energy and momentum is difficult. Certainly, phonons have been argued to play a large role in the normal state self-energy (213), particularly at low dopings where polaronic effects are evident (218), but it is a stretch to believe that phonons are responsible for d-wave pairing at the high temperatures observed in the cuprates, though some have advocated this (219).

What should be remembered is that ARPES for overdoped materials (where the complications of a pseudogap are not present) is consistent with an energy gap of the functional form $\cos(k_x a) - \cos(k_y a)$ (141; 220). This implies pairing originating from near neighbor copper interactions (since this function is the Fourier transform of such). It is doubtful whether phonons would give rise to this particular functional form - or intra-unit cell orbital currents for that matter, where the pairing vertex is of the form $(\mathbf{k} \times \mathbf{k}')^2$ (221). Spin fluctuations can, as well as RVB theories. It has been argued that these latter two approaches represent opposite limits of a more general theory (222), but Anderson has argued against this (223). Certainly, there is a difference between local singlets (RVB) as opposed to longer range antiferromagnetic spin fluctuations. Regardless, the real worry is that as in ^{3}He, everything and the kitchen sink might be contributing to the pairing.

Ultimately, it may take unbiased numerical approaches to settle these matters. Quantum Monte Carlo (QMC) simulations of fermionic systems suffer from the sign problem where negative probabilities occur, meaning that one is limited in how low in temperature one can do reliable calculations. QMC simulations of the single

band Hubbard model remain inconclusive - some indicate superconductivity, others not (224). Another essentially exact approach is the density matrix renormalization group (DMRG) approach (225), but extending this to two dimensions requires simulating finite width strips (226). Such simulations do indicate stripe formation (227), but have yet to say anything definitive in regards to pairing, at least for the square lattice case (as opposed to ladders). Approximations to DMRG have been developed for 2D, including PEPS (projected entangled pair states) (228) and MERA (multiscale entanglement renormalization ansatz) (229), which attempt to preserve certain correlations during coarse graining, but the general efficacy of these methods for the question of superconductivity has yet to be demonstrated.

Perhaps the most popular approach has been dynamical mean field theory (DMFT) (230) and its various cluster extensions (either in momentum space or real space). This involves attempting to do a solution of the 'exact' problem for a cluster, and then embedding this cluster in a bath, with the bath-cluster interaction treated by hybridization as in an Anderson impurity model, in order to represent the full periodic system. Typically, a quantum Monte Carlo solver is used, again limiting one in the temperature range that can be accessed, though ironically, this is less a restriction for pairing since the bosonic nature of the pair state somewhat ameliorates the sign problem (231). Clusters up to 16 sites have been treated, though it will take larger clusters to verify convergence in regards to symmetry breaking ground states such as magnetism or superconductivity. As mentioned above, four site clusters are consistent with singlet formation á la RVB (205), though it is now recognized that such clusters overemphasize singlet formation. Still, DMFT methods have evolved to the point where they can now explain quantitative trends in the cuprates, such as the variation of T_c with various on-site and hopping energies, including the important role of the apical oxygens (232).

The most recent DMFT results indicate that the pseudogap is a precursor of the Mott insulating gap at zero doping, and as it is suppressed, superconductivity appears. Since this gap primarily affects states near $(\pi, 0)$ (antinodal states), the unusual nodal-antinodal dichotomy revealed by photoemisson, where nodal states are gapless and coherent, and antinodal states gapped and incoherent, is naturally explained (233). This gives new insight into the nature of the Fermi 'arcs', and follows earlier speculations by Bob Laughlin that the pseudogap seen in ARPES extrapolates to the Mott gap as the doping is reduced (234). This approach is also in line with the basic RVB idea that the large superexchange J that is a unique signature of cuprates is the source of pairing, though again, detailed calculations of the anomalous self-energy give results more reminiscent of spin fluctuation theory (204). In that context, it should be remarked that RVB is usually presented in a 'mean field' approximation. One approach to go beyond this is by including gauge fluctuations (to capture the constraint of no double occupation) which does introduce significant low energy dynamics (235), but whether this is a controlled approximation is unclear.

Regardless, it appears that magnetic correlations of some sort are responsible for d-wave superconductivity in the cuprates. Whether this should best be thought of as singlets, paramagnons, orbital currents, or a combination thereof remains to be seen. Mott physics certainly plays a role, though it should be remarked that overdoped cuprates emerge from a more or less normal Fermi liquid phase. But even if this is so, describing the wealth of phenomena that has been revealed by such techniques as angle resolved photoemission, neutron and x-ray scattering, and scanning tunneling microscopy will keep researchers busy for many years to come.

V. ORGANIC SUPERCONDUCTORS

Although most organics are insulators, some can be metallic. Interest in the possibility of superconductivity goes back to 1964 when Bill Little proposed that such materials could be high temperature superconductors (236). This promoted a flurry of activity, including even a conference, leading Bernd Matthias to once quip that this was the first one he knew that was devoted to non-existent materials (237). But in 1980, the real deal was reported by Denis Jerome's group in a quasi-1D Bechgaard salt (238), followed up by its discovery in quasi-2D variants (239; 240). A nice review of this field recently appeared (241).

A typical example of the quasi-1D variant is $(TMTSF)_2PF_6$. At ambient pressure it exhibits a spin density wave, probably due to Fermi surface nesting, that onsets at about 12K. Under pressure, the SDW is suppressed, after which superconductivity appears at about 1K. These materials exhibit upper critical fields far in excess of the Pauli limiting field, indicating (at least at high fields) that the pairing is triplet in nature.

Perhaps of more interest are the quasi-2D variants, which exhibit superconductivity up to 13K. Typically, these materials are composed of molecular dimers which form a triangular lattice, with one spin 1/2 degree of freedom per dimer. Such frustrated lattices were the original source of inspiration for Anderson's RVB theory (144). Based on this, there has been a lot of interest in the phase diagram of these materials. Of recent relevance is κ-$(ET)_2Cu_2(CN)_3$ (242). At ambient pressure, the material appears to be a Mott insulator but with no evidence for long range magnetic order, implying the ground state is a spin liquid. Low temperature specific heat measurements are consistent with the presence of a Fermi surface (243), perhaps the long sought after 'spinon' Fermi surface of RVB lore (244), though it should be remarked that a transition of unknown origin has been detected at 6K by thermal expansion (245). Under pressure, a superconducting phase appears (246) whose maximum T_c abuts the spin liquid phase (Fig. 24). This phase is

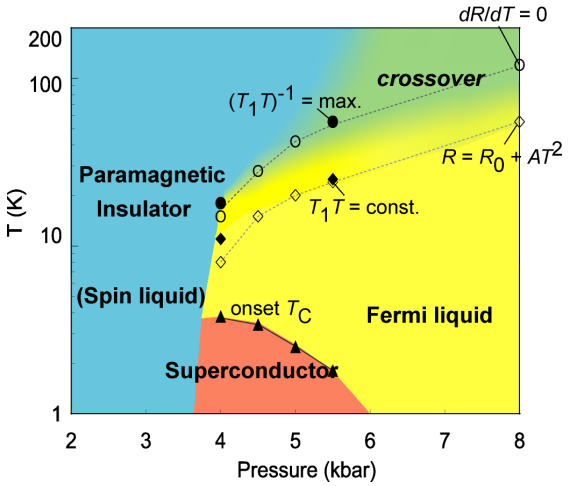

FIG. 24 Phase diagram of κ-$(ET)_2Cu_2(CN)_3$ versus pressure (242). A superconducting phase abuts a Mott insulating phase with no long range magnetic order.

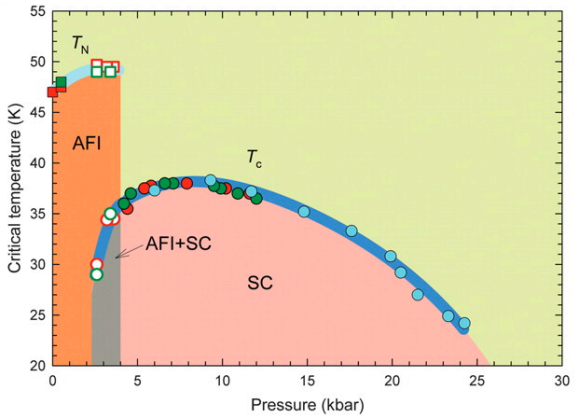

FIG. 25 Phase diagram of Cs_3C_{60} versus pressure (251). Note the presence of an antiferromagnetic insulating phase as in the cuprates.

reminiscent of that seen in underdoped cuprates, with a pseudogap effect apparent in NMR data (241) along with an enhanced Nernst signal above T_c (247).

Little is known about the gap structure of the organics. The NMR relaxation rate varies as T^3 suggestive of nodes (as in the cuprates), though it should be remarked that this T^3 behavior seems ubiquitous in many materials regardless of their nodal structure. Recently, there has been some success with photoemission in this class of compounds (248), so it is hoped in the near future that more definitive evidence of the nature of the superconducting state will be forthcoming. Certainly, the available evidence points to a strongly correlated state, where Mott physics (249) and magnetic correlations play a fundamental role, implying these materials are close cousins of the cuprates.

Besides these materials, a variety of other organic compounds have been discovered which are superconducting. Of particular interest are buckeyballs (C_{60}), which when doped with alkali atoms exhibit superconductivity up to 40 K (250). For a long time, these were regarded as strong-coupling conventional superconductors, but recent work on the 40 K cesium variety (251) indicates a phase diagram again reminiscent of the cuprates and ET salts, where superconductivity emerges under pressure from an antiferromagnetic insulating phase (Fig. 25). Even more recently, high temperature superconductivity has been reported in materials based on chains of benzene rings with superconductivity up to 33 K (252; 253). More work will be necessary in order to understand the relation of these materials to the organic salts described above.

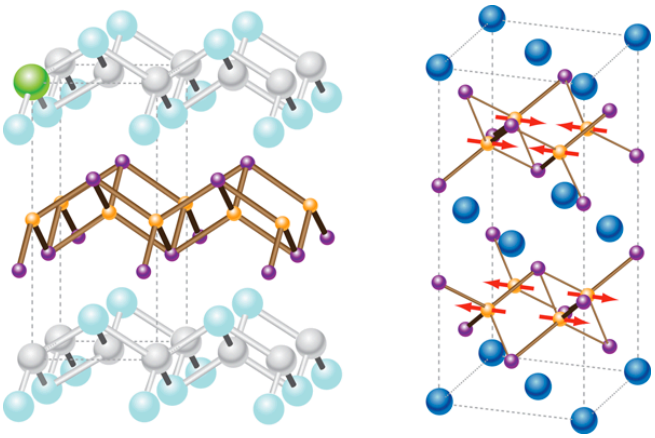

FIG. 26 LaOFeAs (left (259)) and $CaFe_2As_2$ (right (260)) crystal structures, denoted as 1111 and 122 respectively. Yellow are iron atoms, purple are arsenic ones. On the left, a flourine dopant is shown in green. On the right, the spin directions (red arrows) are shown for the magnetic phase.

VI. PNICTIDES

In early 2008, Hosono's group announced the discovery of high temperature superconductivity in an iron arsenide compound (254), following earlier work by this group that had found lower temperature superconductivity in the phosphide variant. Superconductivity was soon seen up to 56 K (255). Several known crystal structure classes have now been identified (Fig. 26), the most studied being the so-called 122 structure (256) which has the same $ThCr_2Si_2$ structure as several heavy fermion superconductors. The materials are composed of square lattices of iron atoms each tetrahedrally coordinated to arsenic ones, though the simpler '11' class of materials are actually iron chalcogenides. FeSe has a relatively lower T_c of 10K (257), though an intercalated version has a T_c above 40K (258).

Like the cuprates, the undoped variant of the arsenides

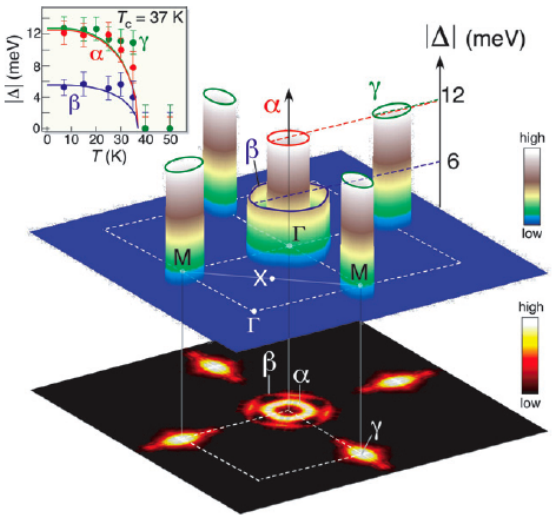

FIG. 27 Photoemission results for potassium doped $BaFe_2As_2$, with the superconducting energy gap denoted as $|\Delta|$. Two hole surfaces occur around Γ and an electron surface around M.

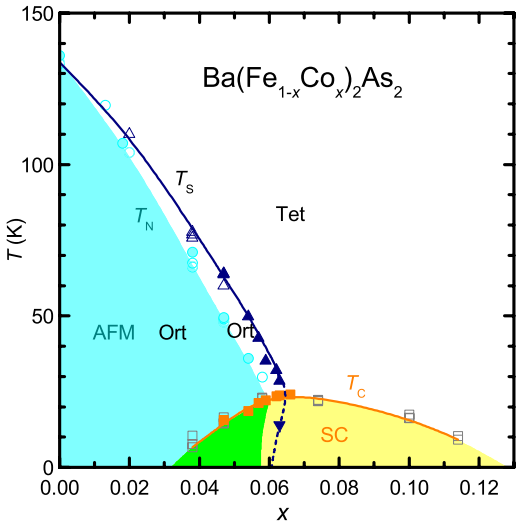

FIG. 28 Phase diagram of cobalt doped $BaFe_2As_2$ (269). T_s denotes the structural transition, T_N the antiferromagnetic one.

is a commensurate antiferromagnet (261), but in the pnictides it is metallic, though ARPES data reveal a Dirac-like dispersion of the electronic states (262) which is consistent with quantum oscillation studies (263). This has led to the general feeling that the ground state is a spin density wave metal driven by Fermi surface nesting as in chromium, though a more localized magnetic picture has been advocated by some (264). Unlike the cuprates, where the spins form a checkerboard pattern, the magnetic order in pnictides is stripe-like instead (261). This is consistent with 'nesting' of the Fermi surface, which is composed of hole surfaces centered at the Γ point and electron surfaces centered at the zone edge (M point), with the separation of these two centers equal to the magnetic ordering vector Q (265) (Fig. 27). The magnetic transition is associated with an orthorhombic distortion of the lattice which usually appears at a slightly higher temperature, though in some materials they are coincident. Sometimes the structural transition appears to be second order, other times first, but intriguingly, a large nematic effect has been identified well above this transition (266).

Upon doping, the magnetic and structural phase transitions are suppressed, and then superconductivity emerges (Fig. 28). Many of the materials indicate a significant range of dopings where the magnetic and superconducting orders co-exist. As in cuprates, a pronounced spin resonance is seen in the superconducting state, as well as a spin gap (267). Unlike the cuprates, where the resonance appears to be a purely triplet excitation (as in cuprates, the pnictides appear to be singlet superconductors), there is evidence that the resonance instead may be a doublet (268). This may be due to the strong anisotropy of the magnetism, where the spin direction tends to be locked to the iron layers.

Given the nature of the Fermi surface, it did not take long for a theory to emerge that suggested the existence of so-called $s_\pm$ pairing (270). This state is a two band generalization of d-wave pairing, where the Fermi surfaces at Γ have an opposite sign for the order parameter than the surfaces at M. The advantage of this state is that it has the required change of sign upon translation by the magnetic ordering vector Q (necessary to obtain a solution in the BCS gap equation for magnetic mediated pairing), yet avoids having nodes, which typically cost energy. This state is consistent with subsequent photoemission studies (271) which indicated relatively isotropic gaps on the Fermi surface (Fig. 27). To date, though, there have only been hints that such a state exists based on phase sensitive measurements (272), though it is certainly consistent with the observation of a spin resonance (267) which implies a sign change of the order parameter under translation by Q.

Since then, a rich variety of information has become available from such probes as NMR, penetration depth, specific heat, and thermal conductivity. Particularly telling has been the magnetic field dependence of the thermal conductivity which indicates an evolution from a nodeless gap to a gap with nodes as the doping increases (273) (Fig. 29). Other measurements indicate nodes or not depending on the material. So far, there has been little evidence for nodes from photoemission, though it should be remarked that pnictides exhibit substantial c-axis dispersion, as evidenced by quantum oscillation studies (274), which means care should be taken with interpretations based on surface sensitive measurements. The strive to address the gap anisotropy question by techniques with better energy resolution has propelled studies using Fourier transformed STM, which although

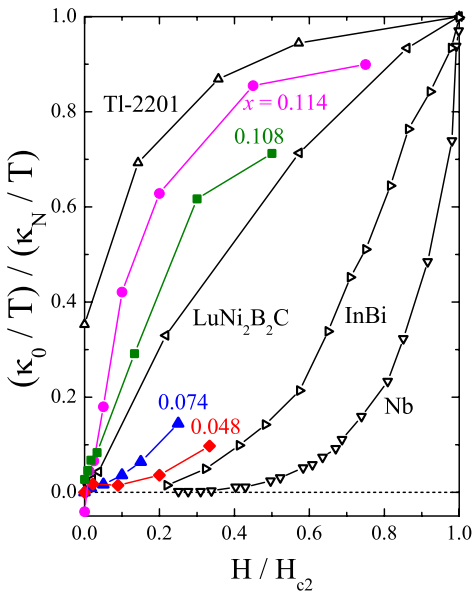

FIG. 29 Magnetic field dependence of the thermal conductivity of cobalt doped $BaFe_2As_2$ (273). Note the evolution from s-wave like behavior (as in Nb) to d-wave like behavior (as in the cuprate Tl2201) as the doping increases.

also surface sensitive, allows the mapping of spanning vectors across the Fermi surface via quasiparticle interference arising from impurity scattering. The most recent study indicates significant gap anisotropy on the Γ centered hole surfaces in LiFeAs (275) but no nodes, which is consistent with photoemission studies (276). An additional advantage of these FT-STM studies is that they can give information on the phase of the order parameter from the magnetic field evolution of the quasiparticle interference pattern, which is consistent with an $s_{\pm}$ state (277).

STM studies also reveal that dopants tend to dimerize (278), which may be related to the nematicity. As this topic has gained much attention of late, it is worth going into in more detail. Transport studies of the pnictides indicate that upon application of uniaxial pressure in the planes, a significant resistivity anisotropy develops above the structural transition temperature (266). This effect gets particularly pronounced at dopings where the structural transition begins to be suppressed. To delve further, it should be remarked that unlike cuprates, in pnictides, band theory predicts that all five of the iron d bands are present in the vicinity of the Fermi energy, and these bands are well separated in energy from the p states of the ligands (279). Nematicity is equivalent to breaking the degeneracy between the x and y directions, which would imply a breaking of the degeneracy of the iron d_{xz} and d_{yz} orbitals. This has now been observed by photoemission, where the polarization dependence of the data allows one to differentiate different d orbitals (280). The most likely explanation of this effect is local orthorhombic order that persists above the structural transition. Since the effect seems stronger than what one would anticipate due to the structure (as in the cuprates), the speculation is that it is either due to orbital ordering as occurs in other transition metal oxides (281) or 'spin' nematicity (282). The latter seems more likely, in that the magnetism and orthorhombicity seem to be intimately related based on the observed phase diagram (Fig. 28). Even band theory studies reveal that the effective exchange constants in the magnetic phase (where one perturbs about the ordered phase) are strong and antiferromagnetic along one in-plane direction and weak and ferromagnetic along the other, consistent with the observed stripe order (283; 284). This pronounced anisotropy is also evident in the spin wave dispersions in the undoped case (285). If a 'spin' nematic picture is correct, this is a further testament that magnetic correlations may be responsible for the pairing.

In that context, there have been many attempts to calculate the pairing microscopically. Early studies seem to rule out an electron-phonon mechanism (286). Most studies have not unsurprisingly indicated $s_{\pm}$ pairing due to magnetic correlations, with some of the more unbiased studies based on the functional renormalization group (FRG) (287). Pairing due to antiferromagnetic spin fluctuations is on more solid ground theory-wise than in the cupratres due to the somewhat weaker correlations in the pnictides. Of course, the on-site U is large for iron, but unlike cuprates, the electrons can somewhat avoid one another by hopping to different d orbitals, leading to a smaller effective U (288). And because of the presence of multiple d orbitals, Hunds rule exchange plays a dominant role as compared to the superexchange J of the cuprates (289). In fact, these findings have led to the quip that pnictides have freed us from the tyranny of Mott physics (290), though there are many in the field that would disagree. Still, RPA, FRG, and DMFT studies are in broad agreement concerning the physics of the superconducting state (291), though there is still some disagreement on how correlated the electrons are and the role of Fermi surface nesting, as well as the doping dependence of the gap symmetry and the importance of spin-lattice coupling in regards to the pairing. Given the wealth of information on how the magnetic correlations, electronic structure, and pairing evolve as a function of doping, it is anticipated that a well accepted theory will emerge in the near future. What is particularly attractive about these materials is that in many cases, the full doping range can be accessed (for instance, $BaFe_2As_2$ - KFe_2As_2) as opposed to the cuprates where superconductivity only exists over a relatively narrow doping range of 20%.

Another attractive feature of pnictides is that in many cases, they exhibit a full energy gap, and also have a relatively weak anisotropy (particularly evident in the directional dependence of the upper critical field). This means that they have the potential of being more technologically relevant than the cuprates, at least in a certain temperature range, though the pnictides unfortunately show the

same 'crashing' of the critical current with grain boundary misalignment as occurs in the cuprates (292). This again may be related to the non-trivial phases associated with $s_{\pm}$ pairing.

VII. OTHER CLASSES

Space prohibits a detailed discussed of other classes of unconventional superconductors, though a few of them are definitely worth mentioning here.

A number of transition metal oxides have the same crystal structure as La_2CuO_4. Of particular interest is Sr_2RuO_4, which exhibits superconductivity at 1.5 K (293). The superconductivity in this case appears to be triplet in nature (294), though there is still much debate on the nature of the order parameter. Phase sensitive measurements are consistent with a sign change of the order parameter when comparing opposite faces (295) and there is evidence as well for time reversal symmetry breaking below T_c (296) which has been taken as support for a $(k_x \pm ik_y)\hat{z}$ pair state. Several complications exist that indicate the order parameter may not be as simple as this. First, three d bands comprise the Fermi surface, as evidenced by quantum oscillation (297) and ARPES studies (298), all sitting near the Brillouin zone boundary, so a simple $k_x \pm ik_y$ form (based on an expansion near Γ) is unlikely. Moreover, if triplet, the d vector structure of the gap has still to be verified, given technical difficulties with obtaining NMR data at low enough magnetic fields, along with the potential issue of field re-orientation of the d vector (299). In that connection, the role of spin-orbit coupling in determining the pair state has yet to be fully elucidated. A detailed discussion of this fascinating material is beyond the scope of this chapter, so the reader is referred to a number of excellent reviews for more information than provided here (299; 300). Certainly, the excitement surrounding strontium ruthenate is not only that it may be the realization of p-wave pairing that had been long sought in materials such as palladium, but because of the chiral nature of the proposed order parameter, it could potentially be exploited for topological quantum computing (301). In that connection, recent experiments are consistent with the existence of half quantum vortices (302).

It was Phil Anderson's great insight in realizing that even in the presence of strong spin-orbit coupling, one could still use parity to classify pair states, and connect this parity with a 'singlet' and a 'triplet' in the degenerate space of k, Pk, Tk, and PTk, where P is the parity operator and T the time reversal one (80). This is not only relevant for heavy fermion superconductors, but potentially for strontium ruthenate as well as mentioned above. But what if parity is broken? This is an old problem going back to magnetic superconductors, since the magnetic structures of antiferromagnets typically break parity symmetry (though they preserve the product of P and T). As mentioned earlier, this should lead to a gap function which is a mixture of a primary even parity component associated with center of mass momentum zero, and a secondary odd parity component with center of mass momentum Q (with Q the magnetic ordering vector) (98). Of course, there is the simpler case where the crystal structure itself breaks parity. In that case, one would assume that even if the primary component of the order parameter was an even parity singlet, an odd parity component could be mixed in. In the past decade, a number of such non-centrosymmetric superconductors have been discovered (303). Space prohibits a detailed discussion of this class of materials, though the interesting ones typically involve ions where spin-orbit coupling is strong. One of these materials is Li_2X_3B with X either Pd or Pt. The Pd case looks singlet in nature and the Pt case triplet (304), though detailed studies of the pairing symmetry as done in the cuprates have yet to be performed. Given their nature, though, non-trivial topological properties of these materials might be realized (305).

This brings us to topological superconductors, a topic of much current interest (306). Topological insulators are variants of normal band insulators where a non-trivial Berry phase exists (307). The effect of this non-trivial phase is the presence of gapless surface states. These have been observed in such systems as Bi_2Se_3 (308). The connection with superconductivity is two fold. First, the prediction that if such materials could be made superconducting, they might exhibit p-wave pairing (309). Cu doped Bi_2Se_3 is superconducting (310), but the jury is still out on the nature of its pairing, though p-wave pairing seems unlikely (the latest tunneling measurements indicate an isotropic energy gap without any in-gap states (311)). The other connection is that if a topological insulator is brought into contact with an s-wave superconductor, zero energy bound states can be induced that behave like Majorana fermions (312; 313; 314), that is, particles that are their own anti-particles. Such fermions could in principle be manipulated for the purpose of topological quantum computing (315). Zero energy bound states have indeed been seen in such hybrid systems (316), but a unique identification of the bound states as Majoranas is a subject of much study and debate (317). Certainly, this is a very active field which is anticipated to yield significant results in the next few years. In that context, p-wave 'spinless' supercurrents have been induced via the proximity effect in half metallic magnets like CrO_2 where the carriers are fully spin polarized (318).

Finally, a number of strong coupling superconductors that are likely s-wave have been identified over the years (319). MgB_2 has a particularly high T_c due to coupling to a particular high energy phonon mode, though it is essentially a conventional superconductor. Shortly after the discovery of cuprates, superconductivity at 30 K was discovered in the perovskite $Ba_{1-x}K_xBiO_3$ (320) following earlier work on the lower T_c lead analogue. A relatively high T_c of 25 K is also seen in a layered sodium doped HfNCl material (321). Recent theoretical work on these

materials is consistent with electron-phonon pairing that is enhanced by strong electron correlations (322). Based on this, there have been recent predictions of related materials that might be superconducting (323). The connections of these materials with unconventional superconductors like the cuprates has been a subject of much speculation.

VIII. EXPERIMENTAL TRENDS

A general observation from the previous sections is that the phase diagrams of unconventional superconductors look remarkably similar in many aspects. Typically, superconductivity is obtained by suppressing some other ordered phase, such as antiferromagnetism. This in turns links these materials to more conventional superconductors such as transition metal dichalcogenides, which typically become superconducting once charge density wave order is suppressed (324). Of course, different orders competing for gapping the Fermi surface is an old observation which is relevant to A15 superconductors as well (325), but the presence of a quantum critical point in the phase diagram associated with the competing order which is typically buried under the superconducting 'dome' is a potentially universal observation that cannot be ignored. This is particularly relevant for those materials which exhibit quantum critical behavior for temperatures above this critical point, which again seems universal to heavy fermions, cuprates, and pnictides. Besides the intriguing prospect of a pairing instability emerging from a non-Fermi liquid normal state, the idea that quantum critical fluctuations are the pairing 'glue' is an appealing concept. This is why there has been so much debate on the nature of the pseudogap phase (198), since it is thought by many that the quantum critical fluctuations associated with the suppression of this state could be the origin of cuprate superconductivity. Whether a universal theory of unconventional superconductivity is possible based on these ideas, and whether this is a large enough 'umbrella' to capture much of the thinking on these materials remains to be seen. Although RVB ideas seem anathema to this line of approach, in some sense, superconductivity from this theory emerges from the suppression of a Mott insulating phase, and so could potentially be captured in this framework as well. Certainly, DMFT simulations are in support of this picture. We will certainly know more along these lines once we have 'nailed' the phase diagram from experiment for various materials and are able to properly correlate them from one class of materials to the next.

The other interesting trend is that certain crystal structures, such as the $ThCr_2Si_2$ one, seem to be amenable to superconductivity. Whether this is an accident or something profound remains to be seen. Certainly, as discussed above for the UX_3 series of compounds, it is interesting that the cubic ones do one thing, but it is the hexagonal variants that exhibit either superconductivity or novel quadrupolar order. Again, as our database of unconventional superconductors grows, the role that the crystal structure plays should become more evident.

IX. THEORETICAL TRENDS

In some sense, we were very fortunate for conventional superconductivity that a unique strong-coupling theory emerged so rapidly after the BCS theory was first proposed. This was to a large part due to the Migdal theorem. In strong coupling electron-phonon systems that are outside of this framework, for instance those exhibiting polaronic effects, there has yet to emerge a similarly robust calculational scheme. For electron-electron pairing, though, all bets are off. Migdal-like approximations have been invoked that attempt to exploit the separation of energy scales between collective and single particle degrees of freedom (326), but the efficacy of this approach has yet to be demonstrated to everyone's satisfaction. This had led to a host of approaches that have been proposed - fluctuation exchange approximation (327), functional renormalization group (328), two particle self-consistency theory (329), large N approaches (330), and dynamical mean field theory in its various cluster versions (331). Each of these methods has their pros and cons. Unlike electron-phonon theories, where we know that there is an attractive interaction (negative electrons, positive ions), in electron-electron theories where the bare Coulomb interaction is of course repulsive, the 'attractive' component is typically of an induced nature, making its evaluation (and even its sign!) a highly non-trivial process. Anderson has advocated that in RVB theories, a 'glue' does not exist (203), that is, there is no induced interaction, with J itself being the pairing interaction. On the other hand, most implementations of this theory have been done at a mean field level. Variational Monte Carlo simulations have been done which give very intriguing results in support of the basic conjectures of this theory (332), but these simulations are biased by nature. Gauge theory approaches have been advocated which brings in dynamics (235), but whether this represents a systematic approximation has been questioned. Certainly, recent developments in quantum Monte Carlo and DMRG methods are promising in regards to giving unbiased results. Coupled with other approaches, for instance cluster DMFT, there is some promise that results will emerge that will generally be accepted by the community.

However, the potentially non perturbative nature of this problem has led to the realization that new approaches might be needed to ultimately solve the problem of unconventional superconductivity. In that sense, the recent attention given to holographic theories is worth commenting on. Strong coupling gauge theories in the context of particle physics has been notoriously difficult to come to grips with. This led to the Maldacena conjecture (333). This conjecture is based on mapping a

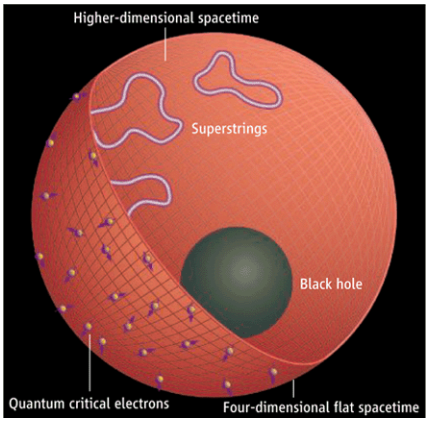

FIG. 30 A schematic representing the anti de Sitter (AdS) - conformal field theory (CFT) duality (337). Quantum critical electrons on the boundary of an AdS space-time are mapped to a weak coupling gravity dual in the interior. The black hole sets the charge density and temperature of the theory.

strong coupling gauge theory that exists on the boundary of a fictitious space-time to a weak-coupling gravitational theory in the bulk (Fig. 30). The space-time in question is anti de Sitter (AdS) space, which is hyperbolic in nature. The extra coordinate in this space-time can be thought of as the coordinate along a renormalization group flow, where one flows from ultraviolet at the boundary to infrared in the interior. To represent a charged system at non-zero temperature, one can simply put a black hole in this space. In the condensed matter context in two dimensions, one typically flows from an AdS_4 geometry near the boundary to an AdS_2 times R_2 one near the black hole horizon (334). The net result is local quantum criticality, since the spatial R_2 part has essentially decoupled (AdS_2 being dual to CFT_1, a conformal field theory in time). In that sense, it is similar to the Kondo problem, which is local in space and critical in time (335). By changing various parameters of the theory, one can tune from a Fermi liquid to a marginal Fermi liquid to a non Fermi liquid (334). Introduction of a scalar field can lead to Bose condensation, thus 'holographic' superconductivity (336). Given certain stability conditions of a scalar field in an anti de Sitter spacetime near a black hole, this condensation is dependent on the black hole horizon, and thus the temperature, therefore one can get a second order phase transition as a function of temperature just as in a real superconductor.

Although this approach is truly non perturbative in nature, for most applications, the theory is essentially at the Ginzburg-Landau level. That is, one assumes a scalar field. Since it is a scalar, it should correspond to some charge $2e$ field, but since the theory does not explicitly invoke pairing, extra terms have to be added to the action to describe the coupling of fermions to the scalar field (i.e, to generate a Bogoliubov dispersion). One neat aspect is that this coupling is dependent on the geometry of the problem (which changes from AdS_2 times R_2 to AdS_4 once the scalar field condenses), and thus one can get the same 'peak-dip-hump' structure observed by photoemission for the antinodal spectral function of the cuprates, basically since the fermion damping is gapped outside an $\omega - k$ 'light cone' determined by the geometry (338). On the other hand, since these are in essence phenomenological considerations, this does not bring real understanding to the problem, since there are a variety of physical effects that can give rise to such a lineshape (including trivial effects like bilayer splitting). Perhaps in the end, these approaches will help to resolve issues connected to the gauge theory approaches used for both the Kondo problem (335) and RVB theories (235). These theories are non-trivial since the gauge fields involved are associated with constraints, and thus differ in fundamental ways from the gauge theories quantum field theorists typically study (339).

X. THE FUTURE

As Yogi Berra supposedly quipped, "It's tough to make predictions, especially about the future". Still, given developments in superconductivity over the past several decades, it is worth giving it a shot. First, given the number of new classes of materials discovered in the past thirty years or so, many of them not touched on here (340), it is pretty certain that new classes of unconventional superconductors will be discovered in the near future. And given the fact that a number of these classes have high T_c, it is pretty certain as well that new high T_c materials are in the offing, though it is unclear whether we will ever beat the cuprates in T_c (at least, under earth like conditions - witness the possibility of ultra high T_c in metallic hydrogen (341)). Most of these discoveries will certainly be serendipitous, though there is hope with the development of layer by layer synthesis, for instance by molecular beam epitaxy, that one might 'design' superconductors (342). But as in the old days, a lot of the discoveries will be by people following their nose, as Muller did for cuprates, and Hosono for pnictides. In that context, there have been recent speculations that doped iridium oxides will be superconducting because of the large value of the exchange integral (343), but to date, this prediction has yet to be verified.

The other matter to comment on is theory. As numerical techniques continue to improve, more and more will be known about non-trivial many body theories from 'exact' techniques like quantum Monte Carlo, and DMRG and related approaches. Moreover, the evolution of cluster DMFT into a predictive tool for superconductivity (232) is a very welcome development. In the end, though, it will take rigorous solutions to convince the skeptics that the results are not due to some sort of calculational bias (i.e., by making the assumption that the model actually has a superconducting ground state to being with). After all, there are few exact theories we know of superconductivity outside of the electron-phonon model. The

Kohn-Luttinger theory comes to mind (344), though this predicted instability of the normal state only occurs at very low temperatures.

Finally, it could well be that 'materials genome' databases might yield new predictions via data mining (345), assuming one is using valid search criteria. That is, that one is not operating in the GIGO (garbage in, garbage out) mode. Certainly, the phase space of materials to explore is astronomical, and it will definitely take a lot of imagination, both from theory and experiment, to explore its infinite richness.

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